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RECENT DISCOVERIES IN CHEMISTRY.

BEING A SECOND SUPPLEMENT TO

WATTS'S DICTIONARY OF CHEMISTRY.

BRINGING THE RECORD OF

CHEMICAL DISCOVERY DOWN TO THE YEAR 1873.

By HENRY WATTS, B.A. F.R.S. F.C.S.

Assisted by eminent Scientific and Practical Chemists, Contributors to the Dictionary.

This Supplement brings down the record of Chemical Discovery to the end of the year 1872, including the more important discoveries published in 1873 and 1874.

The Author states in his Preface that he has again been favoured with the co-operation of two of the former Contributors to the Dictionary, namely, Professor G. C. FOSTER, F.R.S. and Professor ROSCOE, F.R.S. and that he has been able to add to the list the names of three other gentlemen—Dr. H. E. ARMSTRONG, Dr. H. HEWELL MARTIN, and Mr. R. WARINGTON—who have contributed articles of great interest and importance.

Amongst the subjects treated in this supplementary volume the following may be mentioned as deserving of special notice:—

Physical and General Chemistry. The article 'Chemical Action' contains an account of the important researches of BERTHELOT on the State of Salts in Solution, and of those of FAVRE and VIALON on the Decomposition or Dissociation of Crystalline Salts in Solution. The article 'Heat' includes a description of PUNSEN's Ice-calorimeter; a summary of the results obtained by THOMSEN and by MARIGNAC on the Specific Heats of Bodies in solution, and of the extensive and important researches of THOMSEN and of BERTHELOT on the Heat developed in Chemical Action. Under 'Explosion' are given the results of recent investigations made in this country by Mr. ABEL, and in France by BERTHELOT, and by CHAMPION and BELLET on the conditions which determine the Explosive Force of Powder and other Detonants, on the dependence of Explosion on Vibration, and on its transmission at a distance; and under 'Gunpowder' the very important experiments lately published by Captain NOBLE and Mr. ABEL on the Products of Combustion of Powder, and on its Explosive Force when fired under various conditions. The article 'Electricity' contains an account of BACQUEVELL's Researches on Electro-capillary Action, of QUINCE's General Theory of Electrolysis, and of FAVRE's Researches on the Heat developed in the Voltaic Current. 'Magnetism,' by Prof. FOSTER, gives the results of recent investigations on the exact measurements of the Magnetic Forces. 'Light' includes the continuation of Dr. GLADSTONE's researches on Refraction and Dispersion, together with many interesting results of recent investigations on Absorption, Fluorescence, and Circular Polarisation. Dr. ROSCOE has kindly contributed an article on the 'Chemical Action of Light,' including a description and figure of his new Self-recording arrangement for the measurement of this action: and another on 'Spectral Analysis,' giving an account of the most recent investigations on the subject.

2. Inorganic Chemistry. Among the numerous articles belonging to this department of Chemistry, special mention may be made of those relating to the Chlorine-

SECOND SUPPLEMENT to WATTS's Dictionary of Chemistry

compounds of Phosphorus and Sulphur; to SCHÜTZENBERGER's researches on the Carbonyl-compounds of Platinum, and on the Phospho-platinic Compounds; and of CLAYE on the Ammoniacal Compounds of Platinum; and to SIEMEN'S method of preparing Malleable Iron and Steel directly from the Ore.

3. *Organic Chemistry.* Belonging to this department are several articles relating to the interesting discoveries of SCHORLEMMER on the Paraffins and Isomeric Alcohols and Ethers derived from them; also VON MEYER's researches on the Nitroparaffins, and the discovery of a new class of acids called Nitrolic Acids. The Isomerism of the Derivatives of Benzene is discussed in numerous articles, and especially in a highly important and elaborate article by Dr. ARNOLD on 'Benzene' and their derivatives, including the most recent additions to our knowledge of these bodies.

4. *Physiological Chemistry.* A series of interesting articles relating to this department of Chemistry, viz. 'Digestion,' 'Gastric Juice,' 'Glycogen,' 'Muscular Tissue,' 'Proteids,' 'Respiration,' and 'Urine,' has been communicated by Dr. H. R. MARTIN, of Christ's College, Cambridge.

5. *Agricultural Chemistry.* In this department Mr. R. WARINGTON contributes a very valuable series of articles, viz. 'Fodder-plants,' 'Maize,' 'Malt,' 'Manure,' 'Millet,' 'Oats,' 'Root-crops,' including a large amount of original information kindly communicated by Messrs. LAWES and GILBERT, relating to the results of recent investigations at Mr. LAWES's experimental farm at Rothamsted.

OPINIONS of the PRESS.

'The Dictionary of Chemistry, edited by HENRY WATTS, is one of the most valuable contributions to chemical science of which this country can boast, and it is only an act of justice, such as we might reasonably expect, that its Publishers should from time to time issue supplements giving the changes and new discoveries in the science, instead of forcing the purchasers of a valuable and necessarily expensive book to buy new editions or fall behind in their information. It is only about three years since the completion of the last of the five volumes comprising the Dictionary as first published; but such rapid strides are made in chemistry, that in order to record the changes and discoveries, a Supplement of over eleven hundred pages is required. Of course, it is impossible from such a work to quote any passage to show its merits; but the Dictionary is so well known to chemists that they will readily believe us when we say that in the SUPPLEMENT there is even an increase in that careful and laborious editorial work so absolutely necessary to make a book of this kind a standard of reference.'

SCHÖRMANN.

'To afford a complete and accurate view of the contents of a dictionary is

extremely difficult, however full a notice may be given of it; and this difficulty is certainly not diminished when it is a SUPPLEMENT expressly written to record the progress of the science of chemistry since the publication of a work generally admitted to be exhaustive at the date of issue. The SUPPLEMENT extends over 1,136 closely-printed pages, and may therefore be regarded as forming a monument to the progress of the science within the past few years, and to the industry of the author of the record. . . . From this outline of the article on Inorganic Analysis by Flame Reaction, it will at once be seen that the subject is treated in an exhaustive and thoroughly practical manner, yet this forms but one of almost innumerable articles of equal utility and interest. The SUPPLEMENT alone contains an amount of information, compressed into a comparatively small space, which is really marvellous, and, regarded as part of the Dictionary, will make the entire work as nearly perfect as need be desired. It may well be regarded as a good substitute for the most judiciously selected chemist's library that could be purchased for the price at which the whole six volumes are published.'

MINING JOURNAL.

PREFACE.

THE PRESENT SUPPLEMENT brings the Record of Chemical Discovery down to the end of the year 1877, including some of the more important discoveries which have appeared in 1878. As it comprises a longer interval than the preceding Supplements, and is therefore necessarily larger, it will be published in Two Parts.

The Author has great pleasure in acknowledging the assistance of the following gentlemen, who have contributed Articles to the First Part:

E. J. MILLS, D.Sc., F.R.S., 'YOUNG' PROFESSOR OF TECHNICAL CHEMISTRY IN ANDERSON'S COLLEGE, GLASGOW:

Cumulative Resolution.

T. E. THORPE, Ph.D., F.R.S., PROFESSOR OF CHEMISTRY IN THE YORKSHIRE COLLEGE OF SCIENCE, LEEDS:

Cube.

R. WARRINGTON, Esq., F.C.S.:

Harley.—Forest Trees.

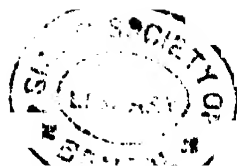
For the Second Part contributions have been kindly promised by DR. ARMSTRONG, F.R.S., 'On Naphthalene and its Derivatives,' 'On Phenols,' and 'On Substitution'; by DR. FLIGHT of the Mineral Department, British Museum, 'On Meteorites'; by PROFESSOR G. C. FOSTER, F.R.S., 'On the Dynamical Theory of Heat'; by DR. ROSCOE, F.R.S., 'On Spectral Analysis'; by DR. THORPE, F.R.S., 'On Specific Volumes,' and 'On Water'; and by MR. WARRINGTON, 'On Wheat.'

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ALLIED BRANCHES OF OTHER SCIENCES.

HENRY WATTS, B.A., F.R.S., F.C.S.

EDITOR OF
'THE JOURNAL OF THE CHEMICAL SOCIETY.'

ASSISTED BY EMINENT CONTRIBUTORS.

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THIRD SUPPLEMENT.

PART I.

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DICTIONARY OF CHEMISTRY.

THIRD SUPPLEMENT.

A

ABSINTHOL, $C^{10}H^{16}O$ (Beilstein a. Kupffer, *Deut. Chem. Ges. Ber.* 2. 1183; Wright, *Chem. Soc. Jour.* [2], xii. 1, 319). This substance, isomeric with ordinary camphor, is the essential constituent of wormwood oil, in which it is associated with a terpene, boiling below 160° , and a deep blue oil which boils between 270° and 300° , and agrees in its properties with the blue chamomile oil examined by Kachler (*1st Suppl.* 277). Absinthol boils at 195° (Beilstein a. Kupffer); at 200 – 205° (Wright); 217° (Gladstone). It differs essentially from camphor in its chemical reactions, not being converted into camphoric acid by oxidation with nitric acid, or into camphocarbonic acid (*1st Suppl.* 385), by the action of sodium and carbonic anhydride, and yielding, when fused with potash, a large quantity of resin, but no acid. Heated with phosphorus pentasulphide, it yields a considerable quantity of cymene, $C^{10}H^{14}$, identical with ordinary cymene from camphor or from cumin oil in density (0.8707 at 0°), boiling point, 175° (Beilstein a. Kupffer), 176° (Wright), and the properties of the sulphonic acid derived from it. Cymene is also formed, though in smaller quantity, together with water and a resinous body, by treating absinthol with zinc chloride. The action of phosphorus pentasulphide on absinthol likewise produces thio-cymene or cymylsulphhydrate, $C^{10}H^{14}SH$, boiling at 233 – 240° (Wright).

For the optical properties of absinthol, see *2nd Suppl.* p. 872.

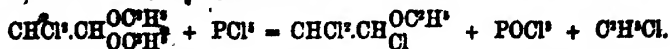
ACEDIAMINE, $C^2H^4N^2$. The existence of this base, discovered by Strecker, has been called in question by Tawildarow (*2nd Suppl.* 1). An analogous base, $C^2H^{10}N^2$, has however been obtained, together with thio- α -toluylamide, $C^8H^8S.NH^2$, by the action of hydrogen sulphide on benzyl cyanide (Bornthsen, *Deut. Chem. Ges. Ber.* viii. 1319). This base is actually xylenyl-amimide, $C^8H^7\begin{smallmatrix} NH \\ NH^2 \end{smallmatrix}$ or $C^8H^7-CH^2-C\begin{smallmatrix} NH \\ NH^2 \end{smallmatrix}$, just as acediamine itself is ethenyl-amimide, $C^2H^3\begin{smallmatrix} NH \\ NH^2 \end{smallmatrix}$. (See XYLENYL COMPOUNDS.)

See NAPHTHALENE-DERIVATIVES.

ACETAL, $C^4H^{10}O^2 = CH^3-CH(OC^2H^5)^2$. On the action of this body on urethane, see CARBAMATES.

Chloroacetal.—According to O. Krey (*Jenaische Zeitschrift*, x. 84), mono-, di-, and trichloroacetal are best obtained by treating a mixture of 2 parts of absolute alcohol and 2 parts of water with 3 parts sulphuric acid and 3 parts of manganese dioxide, distilling off two-thirds of the liquid, and treating the cooled distillate with chlorine till it begins to be turbid. Monochlor- and dichlor-acetal are colourless liquids of agreeable odour, boiling at 154 – 159° and 180° respectively, as stated by Petersen. Trichloroacetal crystallises in large white needles, which melt at 83° and begin to decompose at 190° .

Dichloroacetal and Phosphorus Pentachloride.—These bodies act upon each other in the manner indicated by the equation—



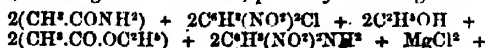
The first of these products is analogous to the compound of aldehyde and ethyl which Wurtz and Frapollin obtained by the action of hydrogen chloride on Acetone.

a mixture of aldehyde and alcohol (*Liebig's Annalen*, cviii, 223). It is intermediate between dichloroacetal and the compound $C^2H^2Cl^4$, which Paternò obtained by the action of phosphorus pentachloride on dichloroaldehyde (1st *Suppl.* 76).

ACETALDEHYDE. See ALDEHYDE.

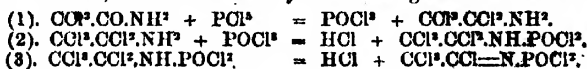
ACETAMIDE, $C^2H^3ONH^2$. Action of PCl^3 .—According to Henke (*Ann. Ch. Pharm.* cvi, 273) phosphorus pentachloride acts on acetamide with great violence, producing a compound of acetonitril with phosphorus trichloride. Wallach, on the other hand (*Deut. Chem. Ges. Ber.* viii, 304), finds that this is not the case, and thinks that Henke must have worked with impure materials. The pure dry compounds act on each other in the cold, only a small quantity of acetamide hydrochloride being formed; if the reaction takes place in chloroform, it becomes violent, but the product is the same, and when the amide and pentachloride are heated together for some time, they yield acetonitril, together with phosphorus trichloride and oxychloride.

Acetamide heated to 150° in a sealed tube with α -dinitrochlorobenzene ($Cl : NO^2 : NO^2 = 1 : 2 : 4$), *magnesia usta* and alcohol, yields ethyl acetate, dinitraniline, and magnesium chloride, probably according to the equation—



The decomposition is, however, very imperfect, a considerable proportion of the dinitrochlorobenzene remaining unaltered (Willgerodt, *Deut. Chem. Ges. Ber.* viii, 1717).

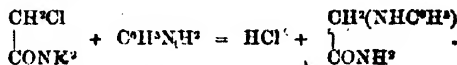
Trichloroacetamide and phosphorus pentachloride heated together yield the compound C^2Cl^3ONP , which appears to have the constitution of hexachlorothidene-imidophosphenyl, $CCl^3.CCl=N.POCl^2$, and to be formed by the following series of reactions:—



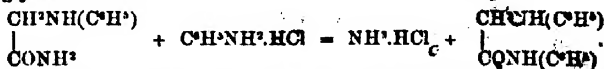
This compound distils at 255° – 259° , and solidifies at 70° – 80° to a white crystalline mass. Its vapours violently irritate the eyes and mucous membranes. It is a very unstable body, which cannot be kept without change. Its decomposition yields trichloroacetonitril, together with other products (Wallach).

Monochloroacetamide, $NH^2.C^2H^3ClO$.—According to P. J. Meyer (*Deut. Chem. Ges. Ber.* viii, 1153), the easiest way of preparing this compound is to pass ammoniac gas into cooled ethyl monochloroacetate: after about an hour's action, the whole of the liquid solidifies to a crystalline cake, while the alcohol formed at the same time contains but a small quantity of the undecomposed ether, which may be treated in the same manner.

One mol. chloroacetamide and 1 mol. aniline cautiously heated together till the amide fuses, and a strong reaction of hydrochloric acid becomes perceptible, yield phenylamidacetamide, phenylamidoglycollamide, or phenylglycocinamide, $CH^3(NH.C^6H^5)CONH^2$, which crystallises from hot water in microscopic needles melting at 133° :—

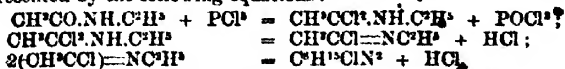


When 2 mols. aniline are heated with 1 mol. chloroacetamide, the action begins in the same manner; but the aniline hydrochloride thereby produced acts further on the phenylamidacetamide, producing phenylamidacetanilide, phenylamidoglycollanilide, or phenylglycocinanilide:



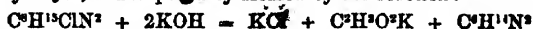
Toluidine acts on chloroacetamide in a similar manner, forming tolylamidoglycollamide, or tolylamidoglycollanilide, according to the proportions used. (See GLYCOLLAMIDES).

Ethylacetamide, $C^2H^3O.NH(C^2H^5)$. This body treated with phosphorus pentachloride yields the hydrochloride of a chlorinated base, which forms with platinum chloride a salt having the formula $(C^2H^3ClN^2.HCl)_2.PtCl^4$. The formation of this base is represented by the following equations:—



Neither the base itself nor the intermediate products have as yet been isolated.

When the crude product of the reaction between ethylacetamide and phosphorus pentachloride is precipitated with potash, and the precipitate is warmed with solid potash, a violent reaction takes place, potassium chloride separates, and a new base, $C^6H^5 \cdot N^2$, is produced in the form of an oily body, miscible with water, alcohol, and ether, and strongly basic, its aqueous solution precipitating most salts and dissolving precipitated alumina. This compound is *ethenyl-diethylamidide*, $CH^3 \cdot C \begin{smallmatrix} \nearrow NC^2H^5 \\ \searrow NHC^2H^5 \end{smallmatrix}$, the first ethenyl-base of the fatty series, and is probably formed by the reaction:

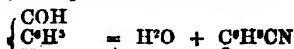


(Wallach & M. Hoffmann, *Deut. Chem. Ges. Ber.* viii. 1567).

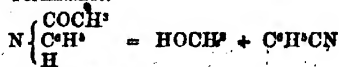
Phenylacetamide or **Acetanilide**, $C^6H^5 \cdot O \cdot NH(C^2H^5)$. This compound heated with *sodium phenate* yields acetone, diphenyl, aniline, and a small quantity of diphenylamine (Weith, *Deut. Chem. Ges. Ber.* vi. 966).

Brakebusch (*Inaugural dissertation*, Göttingen, 1873) states that acetanilide treated with hydrochloric acid is converted into tolunitril. According to C. L. Jackson, however (*Deut. Chem. Ges. Ber.* viii. 1170), this is not the case. When a solution of acetanilide in hydrochloric acid was distilled in a stream of hydrochloric acid gas, no oily distillate was obtained, as described by Brakebusch; and the residue in the retort consisted only of aniline hydrochloride. When the liquid was distilled in a stream of aqueous vapour, acetic acid and aniline hydrochloride were obtained, without a trace of a nitril. Neither any nitril produced by the action of other dehydrating agents on acetanilide. With *sino chloride* the compound $(C^6H^5 \cdot NH^2) \cdot ZnCl^2$ was formed, which, when strongly heated, yielded a viscid oil containing aniline, but no nitril. With *calcium chloride* similar results were obtained. Acetanilide heated with *phosphoric anhydride* was for the most part carbonised.

The behaviour of acetanilide with dehydrating agents is therefore different from that of formanilide, which, as shown by Hoffmann (*Ann. Ch. Pharm.* cxlii. 121), is thereby partially converted into benzonitril. This difference of behaviour is quite in accordance with the difference in composition of the two bodies:



Formanilide.



Acetanilide.

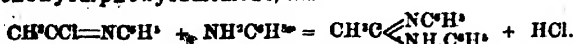
Formanilide splits up directly into water and benzonitril; similarly acetanilide might split up into methyl alcohol and benzo- (not tolu-) nitril; if, on the other hand, it were actually to yield water, the remainder would probably be a body having the constitution $N \begin{smallmatrix} \nearrow C^6H^5 \\ \searrow C=CH^3 \end{smallmatrix}$.

Acetanilide heated with *phosphorus pentachloride* is converted into ethenyl-diphenyldiamine, $C^6H^5 \cdot N^2 = N^2 \begin{smallmatrix} \nearrow (C^6H^5) \\ \searrow (C^6H^5) \end{smallmatrix}$ or $CH^3 \cdot C \begin{smallmatrix} \nearrow NH \cdot C^6H^5 \\ \searrow NH \cdot C^6H^5 \end{smallmatrix}$ (Lippmann, *Deut. Chem. Ges. Ber.* vii. 541).

On the other hand, when pure and dry acetanilide is shaken together with finely triturated phosphorus pentachloride, rise of temperature being prevented, a pale-yellow liquid is formed, which on standing deposits crystals of acetanilide-chloride:—

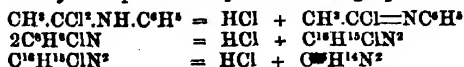


This product is very unstable, and speedily resolves itself into hydrochloric acid and the imide-chloride, $CH^3 \cdot CCl = N \cdot C^6H^5$. The last body acts violently upon *aniline*, forming ethenyl-diphenylamidide, thus:—



Acetanilide-chloride, when carefully heated, melts below 50° and begins to evolve hydrochloric acid; and if then cooled suddenly, to stop further decomposition, it is found to be converted, for the most part, into the hydrochloride of a base having the formula $C^6H^5 \cdot CIN^2$, and crystallising from a mixture of alcohol and ether in small colourless prisms melting at 116° – 117° . This base, when heated above its melting point, assumes a dark colour, and at 140° – 150° a violent reaction suddenly takes place, the result being that it is converted into the hydrochloride of a new base,

which dissolves in water and is thrown down in an amorphous state by alkalis, and forms an amorphous double salt with platinum chloride. The formula of this body has not been satisfactorily determined; but the numbers, obtained by analysis agree approximately with the formula of ethenyl-phenyl-diamine. Its formation from acetanilide-chloride may be represented by the following equations:—



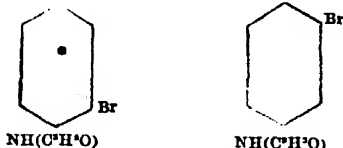
(Wallach a. Hoffmann, *Deut. Chem. Ges. Ber.* viii. 1567).

Derivatives of Acetanilide.

The brominated and chlorinated derivatives of acetanilide admit of metameric modifications, according as the replacement of the hydrogen by the halogen element takes place in the phenyl-group or in the acetyl-group.

Bromophenylacetamides or **Acetobromanilides** (Remmers, *Deut. Chem. Ges. Ber.* vii. 346; Körner, *Gazz. chim. ital.* iv. 329). In these bodies the bromine enters into the phenyl-group.

Monobromophenylacetamide or **Acetomonobromanilide**, $\text{C}^6\text{H}^4\text{Br}\cdot\text{NH}(\text{C}^2\text{H}^3\text{O})$. This compound admits of three isomeric modifications, ortho-, meta-, and para-, according to the relative positions of the bromine and the residue $\text{NH}(\text{C}^2\text{H}^3\text{O})$. The para-



modification is prepared: 1. By the action of acetyl chloride on parabromaniline, $\text{C}^6\text{H}^3\text{Br}\cdot\text{H}\cdot\text{NH}\cdot\text{H}^2$ (Körner). 2. By gradually adding, the theoretical amount of bromine to an acetic acid solution of acetanilide (Remmers). It may also be separated from the product of the action of bromine on acetanilide, suspended in a large quantity of water (which also contains acetodibromanilide and tribromaniline) by pressing the resulting white powder, and dissolving it in hot alcohol, the solution on cooling depositing large crystals of nearly pure acetomonobromanilide, while other fractions may be obtained by gradual evaporation of the mother-liquids. The whole may be purified by recrystallisation from alcohol, the pure acetomonobromanilide crystallising out first (O. Güreke, *Deut. Chem. Ges. Ber.* viii. 114).

This compound crystallises in large many-faced prisms having a vitreous aspect, sometimes perfectly transparent and colourless, sometimes partially or totally opaque and white, with a nacreous lustre. It is moderately soluble in absolute alcohol, and separates therefrom by spontaneous evaporation in unusually fine crystals. It is nearly insoluble in cold water, very slightly soluble in boiling water, and melts at 165.4° (Körner).

Fuming nitric acid converts paracetobromanilide into a nitrobromophenyl acetamide, $\text{C}^6\text{H}^3\text{Br}(\text{NO}^2)\cdot\text{NH}(\text{C}^2\text{H}^3\text{O})$, which crystallises in long sulphur-yellow needles, melting at 102° , and decomposed by soda, with formation of a nitroparabromaniline, which crystallises in yellow needles melting at 112° . Nitrobromophenylacetamide is converted by tin and hydrochloric acid into the hydrochloride of ethenyl-bromo-

phenylene-diamine, $\text{N} \begin{Bmatrix} (\text{C}^6\text{H}^3\text{Br}) \\ (\text{C}^2\text{H}^3)^{\text{y}} \\ \text{H} \end{Bmatrix}$ (Remmers).

Ortho-acetobromanilide, $\text{C}^6\text{H}^3\text{Br}(\text{NH}\cdot\text{C}^2\text{H}^3\text{O})\text{H}^2$, prepared by the action of acetyl chloride on orthobromaniline, crystallises in flat needles, 4 or 5 centimeters long, colourless, transparent, and having a fine satiny lustre. It dissolves in alcohol more easily than the para-compound, and melts at 99° (Körner).

Acetodibromanilide or **Dibromophenylacetamide**, $\text{C}^6\text{H}^2\text{Br}^2\cdot\text{NHC}^2\text{H}^3\text{O}$, is formed by boiling dibromaniline (m.p. 79.5°) for several days with glacial acetic acid, and crystallises in colourless needles or plates melting at 146° . By nitration it yields nitrodibromophenylacetamide, $\text{C}^6\text{H}^2\text{Br}^2(\text{NO}^2)\cdot\text{NHC}^2\text{H}^3\text{O}$, which crystallises in slender yellow needles melting at 209° . This nitro-compound is decomposed by fixed alkalis, with elimination of ammonia and formation of dibromonitrophenol, probably identical with that which Körner obtained by nitrating dibromophenol, and Bruck

by brominating ordinary nitrophenol. Nitrodibromophenylacetamide heated with ammonia to 160° in sealed tubes is converted into nitrodibromaniline, $C^6H^3Br^2(NO^2).NH^2$, which crystallises in golden-yellow needles, melting at 123°, readily soluble in alcohol, but insoluble in water (Remmers).

Acetotribromanilide or *Tribromophenylacetamide*, $C^6H^3Br^3.NH(C^2H^3O)$, is formed by the action of acetyl chloride on tribromaniline, and crystallises in rhombohedrons or long white needles, melting at 232° (Remmers).

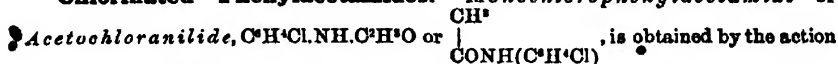
Tribromophenyldiacetamide, $C^6H^3Br^3.N(C^2H^3O)^2$, is formed by heating tribromaniline with acetic anhydride:



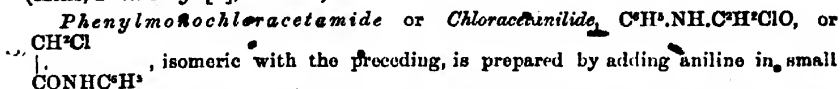
This compound crystallises in long slender colourless needles or rhombohedrons, somewhat soluble in water, easily soluble in alcohol or ether. It melts at 123° and sublimes unchanged at a higher temperature. On boiling it with a solution of caustic soda, one acetyl-group is eliminated and acetotribromanilide is produced (Remmers).

Nitrotribromophenylacetamide, $C^6HBr^2NO^2.NH.C^2H^3O$, forms yellow needles slightly soluble in water, easily in alcohol. *Nitrotribromophenyl-diacetamide*, $C^6HBr^2NO^2.N(C^2H^3O)^2$, is very similar to the preceding compound, and is converted into it by boiling with alkalis. By heating either of these two nitro-compounds with aqueous or alcoholic ammonia in sealed tubes to 180°–220°, nitrotribromaniline, $C^6HBr^2NO^2.NH^2$, is obtained in broad lustrous yellow needles, slightly soluble in alcohol, melting at 214°–215°, and capable of sublimation (Remmers).

Chlorinated Phenylacetamides. *Monochlorophenylacetamide* or



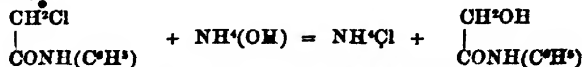
of chlorine on a cold saturated solution of acetanilide, and immediately separates from the solution in crystals, which may be purified by washing with cold water, and once recrystallising from boiling water. Distilled with potash it yields monochloraniline similar in properties to that which is obtained by the action of potash on chlorisatin (Mills, *Phil. Mag.* [4], xix. 21).



quantities to chloracetyl chloride in a cooled vessel, the change consisting in the replacement of an atom of hydrogen in aniline by the group C^2H^3ClO (Tommasi, *Compt. rend.* lxxvi. 885; *Chem. Soc. Jour.* [2], xi. 911). P. J. Meyer (*Deut. Chem. Ges. Ber.* viii. 1153) dissolves the aniline and the chloracetyl chloride in ether before mixing them, and keeps the mixture at a very low temperature.

Chloracetanilide crystallises from water in needles, and from alcohol in plates. It melts at 97°, sublimes at a higher temperature, dissolves freely in ether and acetic acid, easily also on warming in hydrochloric and sulphuric acids. Nitric acid converts it into a nitro compound (Tommasi). According to Meyer, it crystallises in slender microscopic needles, having a silvery lustre and unctuous feel, melting at 134.5°, and subliming without decomposition, emitting at the same time, and likewise when boiled with water, an odour which strongly irritates the mucous membranes; its solution burns the skin violently. It dissolves easily in alcohol, ether, and hot water, sparingly in cold water.

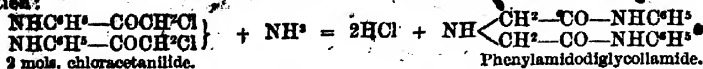
Action of Ammonia.—The mode of action of ammonia on chloracetanilide, as described by Tommasi and by Meyer, appears to differ according to the temperature and the strength of the ammoniacal solution employed.* According to Tommasi, chloracetanilide digested at 30–40° with a saturated solution of ammonia gas in dilute alcohol is converted into phenyl-hydroxylacetamide or hydrox-acetanilide, $C^6H^5.NO^2$:—



According to Meyer, on the other hand, chloracetanilide digested with moderately concentrated alcoholic ammonia in a sealed tube at the heat of the water-bath, for

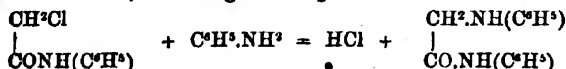
* The wide difference between the statements of these two chemists as to the melting point of chloracetanilide, induces, however, a suspicion that one or the other must have been dealing with an impure product.

several hours, is converted into phenylamidoglycollamide, $C^6H^5N^2O$ formed by the reaction:



In the one case an atom of chlorine in the group CH^2Cl is replaced by OH; in the other the two atoms of chlorine in two such groups are replaced by imidogen NH , which then unites the two groups $\text{NH}(C^6H^5)\text{COCH}^2$.

Chloracetanilide boiled with a slight excess of aniline is converted into phenylamidoglycollanilide; according to the equation:



With toluidine in like manner the product is tolylamidoglycollotoluide, $\text{ClH}^3.NH(C^6H^7)\text{—CO.NH}(C^6H^7)$. See GLYCOLLAMIDES.

Dichlorophenylacetamide or Acetodichloranilide, $C^6H^3Cl^2.NH.C^6H^3O$, or CH^3

$\text{CO.NH.C}^6\text{H}^3\text{Cl}^2$, is formed, together with acetomono-chloranilide, by the action of

hypochlorous acid (solution of bleaching powder acidulated with acetic acid) on acetanilide. With this reagent chlorination takes place instantly, but the mono-chlorinated compound first formed is not further attacked as long as any free acetanilide remains. Either the mono- or the di-chlorinated compound may be obtained pure by the use of measured quantities of hypochlorous acid.

When an excess of hypochlorous acid is used, the product obtained is not acetodichloranilide, but a compound of that body with a molecule of hypochlorous acid, $C^6H^3Cl^2.NH.C^6H^3O + \text{HOCl}$. This compound is a thick heavy oil, of peculiar apricot colour, highly refractive, smelling faintly of chlorine, and having a disagreeable taste. Its density is 1.3893, water at 20° being 1. When quite dry it is moderately stable, but in the moist state or in contact with other bodies of most diverse character, it separates into its constituents. It is but sparingly soluble in water; when boiled therewith it is volatilised and decomposed. It is decomposed by alkalis. Ammonia acts violently upon it even in the cold, nitrogen being set free. Mineral acids attack it with violence. Strong sulphuric acid liberates a gas smelling of chlorine monoxide. Strong nitric and hydrochloric acids evolve torrents of chlorine. It is decomposed also by alcohol and ether; a solution of it in the latter liquid, when exposed to diffused light, gradually deposits crystals of dichloroacetanilide, the ether at the same time acquiring a chlorous odour.

In the decompositions of the oily body, the end-product is always acetodichloranilide. Conversely, the oily body is formed when acetodichloranilide is treated with solution of bleaching powder.

The oil, in virtue of its property of giving up hypochlorous acid, has a certain value as a reagent. With aromatic amines it gives a series of colours analogous to those produced by bleaching powder, but much more intense and lasting. The colouring matters thus produced have however no affinity for animal fibres; silk immersed in them remains perfectly white.

When chlorine is passed into acetanilide as long as it is absorbed, the product is a thick yellow oil, which is usually regarded as acetodichloranilide contaminated with oily products (chlorinated phenols). This oil, when treated with alcohol, yields large quantities of nearly pure acetodichloranilide, and it is violently attacked by potash-ley, likewise with formation of dichloroacetanilide. It is most probably a compound of acetodichloranilide with one molecule of chlorine, analogous to the hypochlorous acid compound above described. A similar body is formed when acetanilide is treated with excess of bromine; moreover, bromine dissolves large quantities of acetodichloranilide with extraordinary facility, forming a thick brown oil (O. N. Witt, *Deut. Chem. Ges. Ber.* viii. 1226).

Phenyl-trichloroacetamide, $C^6H^3.NH.C^3Cl^3O$ (Tommasi a. Moldola, *Chem. Soc. Jour.* [2], xii. 316).—This compound is prepared by gradually pouring rectified aniline into an excess of trichloroacetyl chloride, $C^3Cl^3O.Cl$, heating the mixture, after the first reaction is over, then leaving it to cool, washing the resulting solid mass with water, then dissolving it in hot alcohol, with addition of animal charcoal, and filtering. The filtrate, on cooling, deposits the amide in lustrous crystalline plates, appearing rhomboidal under the microscope. It is nearly odourous, and has a slightly bitter taste, melts at 94° , and solidifies again at 83° . It dissolves readily in cold sulphuric acid, and decomposes without blackening when the solution is heated.

It is soluble also in benzene and turpentine oil, and extremely soluble in carbon sulphide, chloroform, and ether. By boiling with caustic soda it is decomposed, with production of a basic substance having a very pungent odour. The same decomposition appears to take place when the amide is heated in a sealed tube with alcoholic ammonia, or boiled with water.

Dinitrophenyl-trichloracetamide, $C^6H^3(NO_2)_2.NH.C^3Cl_3O$, is produced by heating phenyl-trichloracetamide with excess of fuming nitric acid. The amide at first dissolves, the solution then becomes suddenly hot, and nitrous fumes are copiously evolved. The reaction is completed by heating on a sand-bath, and the solution then poured into cold water. A heavy oil separates, and sinks to the bottom, remaining for some time in a semi-fluid state, but ultimately solidifying to an orange-coloured mass, which is dissolved in hot alcohol, and filtered. The filtrate on cooling deposits dinitrophenyl-trichloracetamide in tufts of yellow needles.

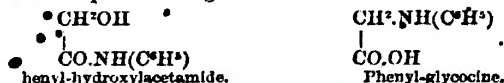
This compound melts at 118° , and remains in a viscid state at the ordinary temperature of the air for some time after fusion. It does not explode on heating. It dissolves to a slight extent in boiling water, giving a solution of yellow colour and slightly acid reaction. Benzene, chloroform, and ether dissolve it readily, oil of turpentine less readily. It is easily soluble in cold caustic soda-solution, a yellow liquid being produced, from which acids reprecipitate the amide unaltered. On boiling the solution, however, it assumes a fine red colour, gives off an odour like that of nitrobenzene, and deposits a yellow substance on cooling (Tommasi a. Meldola).

Phenyl-hydroxyacetamide, $C^6H^5NO_2 = C^6H^5.NH.C^2H^2(HO)O$ (Tommasi, *Chem. Soc. Jour.* [2] xii. 623). This compound, derived from phenyl-chloracetamide by substitution of HIO for Cl , is prepared by heating phenyl-chloracetamide (p. 6) in a long-necked flask fitted with a long narrow condensing tube, and standing in a water-bath, with dilute alcohol (of 30° – 40° B.) saturated with ammonia gas at a temperature of 40° – 50° . After some time a crust of sal-ammoniac forms on the sides of the flask, and goes on increasing for about twenty-four hours. The flask is then removed from the water-bath, and placed in a freezing mixture till the greater part of the remaining sal-ammoniac has crystallised out, and the filtered liquid is mixed with a large quantity of cold water, which separates a very viscid slightly yellowish liquid. This liquid is to be washed with water till all the sal-ammoniac is removed from it, then with aqueous, and finally with absolute alcohol; and the purified product heated for several hours in a water-bath, whereby a thick liquid is obtained, which solidifies in cooling to a slightly yellowish, easily friable mass, somewhat resembling colophony.

This substance dried at 100° gave by analysis numbers agreeing with the formula $C^6H^5NO_2$ or $C^6H^5NO_2 + H_2O$. The molecule of water cannot be removed without partial decomposition of the compound.

Phenyl-hydroxyacetamide begins to melt at 65° and becomes perfectly liquid at 115° . It is insoluble in cold water, and decomposed by boiling water, also by potash, soda, and baryta, with separation of a slightly alkaline oily liquid which exhibits the properties of aniline. It is insoluble in ether, slightly soluble in alcohol; insoluble in hydrochloric acid, even at the boiling heat, also in cold sulphuric acid; but dissolves in hot sulphuric acid, forming a brown solution, which gives no turbidity with water or with aqueous ammonia. It is attacked by hot nitric acid with evolution of red fumes, and the solution mixed with water deposits a copious light yellow precipitate.

Phenyl-hydroxyacetamide is isomeric with phenyl-glycocine, the structural formulae of these two compounds being:



Acetylacetamide or **Acetoluide**, $C^6H^4(CH^3).NH.C^2H^3O$. The para-modification of this compound, oxidised with potassium permanganate, yields an acetamidobenzoic acid, $C^6H^4(NH.C^2H^3O).CO.OH$, which crystallises in needles, sparingly soluble in water, more readily in alcohol, and melting, with partial decomposition, at 250° ; easily converted by boiling hydrochloric acid into hydrochloride of paramidobenzoic acid (A. W. Hoffmann, *Deut. Chem. Ges. Ber.* ix. 1299).

Tolyl-chloracetamide or **Chloracetoluide**, $C^6H^4Cl.NO = C^6H^4Cl-CONH(C^2H^3)$, (Meyer, *Deut. Chem. Ges. Ber.* viii. 1154; Tommasi, *Chem. Soc. Jour.* [2], xi. 911; xii. 628). This compound, called by Tommasi, *Benzyl-chloracetamide* and *Cresylchloracetamide*, is prepared, like the corresponding anilide, by the action of chloracetyl chloride on an ethereal solution of solid toluidine. The

ether is evaporated, the residue repeatedly boiled with alcohol, and the solution mixed with water, which precipitates the chloracetoluide in large plates (Meyer). Tommasi prepares it by adding toluidine in small quantities to chloracetyl chloride in a cooled vessel.

Chloracetoluide crystallises from a very dilute boiling alcoholic solution in white needles, melting at 161.5° (Meyer), at 162° (Tommasi). It sublimes without decomposition—at 110° (Tommasi)—and does not exhibit the unpleasant characters of the anilide. It dissolves in alcohol and ether, easily when hot, sparingly when cold; in water it dissolves but slightly, even at the boiling heat (Meyer). It dissolves in hot sulphuric and acetic acids, but not in hydrochloric acid. With nitric acid it appears to form a nitro-derivative (Tommasi).

With ammonia, aniline, and toluidine, chloracetoluide reacts like chloracetanilide. With alcoholic ammonia it forms, according to Tommasi, tolyl-hydroxylacetamide, $\text{CH}_2(\text{OH})\text{—CONH}(\text{C}_6\text{H}_5)$; according to Meyer, tolylamidodiglycollamide, $\text{NH}\begin{matrix} \text{CH}_2\text{—CO—NH}(\text{C}_6\text{H}_5) \\ \text{CH}_2\text{—CO—NH}(\text{C}_6\text{H}_5) \end{matrix}$. With aniline it forms tolylamidodiglycollanilide, $\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)\text{—CO.NH}(\text{C}_6\text{H}_5)$, and with toluidine, tolylamidodiglycolltoluidide, $\text{CH}_2\text{NH}(\text{C}_6\text{H}_4)\text{—CONH}(\text{C}_6\text{H}_4)$ (Meyer). See GLYCOLLAMIDES.

Tolyl-hydroxylacetamide, $\text{C}_8\text{H}_9\text{NO}_2 = \begin{matrix} \text{CH}_2\text{OH} \\ | \\ \text{CO.NH}(\text{C}_6\text{H}_5) \end{matrix}$, is prepared, like

the corresponding phenyl-compound, by the action of alcoholic ammonia on chloracetoluide. When dried at 120° , it gave by analysis (mean) 56.21 p. c. carbon, 7.44 hydrogen, and 7.15 nitrogen, agreeing with the formula $2\text{C}_8\text{H}_9\text{NO}_2 + 3\text{H}_2\text{O}$. The anhydrous compound has never been obtained. The hydrate is solid at ordinary temperatures, begins to melt at 70° , but becomes perfectly fluid only at 130° . It is insoluble in cold water, but dissolves partially in boiling water, with separation of a small quantity of a white substance, having a greasy aspect, a slight alkaline reaction, and the smell of toluidine. This decomposition is much more easily effected by solution of caustic potash, soda, or baryta; tolyl-hydroxylacetamide is slowly attacked by cold, quickly by warm nitric acid, with formation of a compound which does not dissolve in water. It is insoluble in hydrochloric acid, even concentrated and boiling. It dissolves sparingly in cold, somewhat more freely in hot sulphuric acid, without blackening (Tommasi).

Tolylacetamide or **Acetoxylide**, $\text{C}_8\text{H}_7\text{NH.C}_6\text{H}_5\text{O}$, or $\text{C}_8\text{H}_7(\text{OH})_2\text{NH.C}_6\text{H}_5\text{O}$. When the modification of this compound which melts at $127^\circ\text{—}128^\circ$ is mixed in hot aqueous solution with a concentrated solution of potassium permanganate, a product is formed, which appears to be a mixture of two acids, one of which—easily isolated, as it forms an insoluble copper salt—is a acetamido-phthalic acid, $\text{C}_8\text{H}_4(\text{CO}_2\text{H})_2\text{NH}(\text{C}_6\text{H}_5\text{O})$, (Hoffmann, *Deut. Chem. Ges. Ber.* ix. 1209).

Naphthylacetamide, $\text{C}_{10}\text{H}_7\text{NH.C}_6\text{H}_5\text{O}$ (Tommasi, *Compt. rend.* lxxvi. 1267). Formed by the action of acetyl chloride, acetic anhydride, or better, glacial acetic acid, on naphthylamine. Crystallises in white silky needles, melting at 152° , subliming at 160° , slightly soluble in boiling water, readily in alcohol and in dilute acids. With nitric acid it yields a mixture of nitro-compounds which have not yet been examined.

Naphthyl-chloracetamide, $\text{C}_{10}\text{H}_7\text{NH.C}_6\text{H}_4\text{ClO}$, prepared by the action of chloracetyl chloride on naphthylamine, crystallises in colourless silky needles, which melt at 161° , and are soluble in alcohol and in acetic acid (Tommasi).

ACETENYL-BENZENE, or **Phenyl-acetylene**, $\text{C}_8\text{H}_6 = \text{C}_6\text{H}_5(\text{C}\equiv\text{CH}) = \text{C}_6\text{H}_5\text{—C}\equiv\text{CH}$. This hydrocarbon, prepared by dry distillation of the barium salt of phenyl-propionic acid (1st Suppl. 5), is reconverted into that acid by the joint action of sodium and carbonic anhydride:



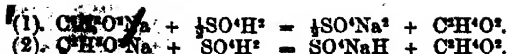
The phenyl-propionic acid thus produced melts at $136^\circ\text{—}137^\circ$, and is identical with that which Glaser obtained from cinnamic acid (Paternò, *Gazzetta Chimica italiana*, ii. 553).

ACETIC ACID. *Formation and Preparation*.—This acid constitutes the lower-boiling portion (below 125°) of the crude fermentation butyric acid, obtained by leaving a mixture of malt, milk, chalk, and minced meat to stand for several weeks (Grillone, 2nd Suppl. 227). According to Béchamp (*Compt. rend.* lxxvi. 836) it is normally present in milk, together with alcohol, as a product of the action of microzymes.

In preparing glacial acetic acid by distilling acetic acid with strong sulphuric acid, some authors recommend the use of 1 equivalent ($\frac{1}{2}$ mol.) hydrogen sulphate to 1 equiv. sodium acetate, whereas others recommend twice that proportion of hydrogen sulphate:—

ACETIC ACID.

9



(See Gmelin's *Handbook*, viii. 287.)

According to F. Mohr (*N. Rep. Pharm.* xx. 28) the smaller proportion of acid, that is to say 4-4½ pts. strong sulphuric acid to 12 pts. dry sodium acetate, is sufficient for the purpose. Hager, on the other hand, maintains that to ensure the complete separation of the acetic acid, without decomposition or formation of sulphurous acid, double that quantity of sulphuric acid must be employed. B. Hirsch (*N. Jahrb. Pharm.* xlix. 270) recommends as the best proportions, 10 pts. by weight of crystallised sodium acetate, 4 pts. of strong sulphuric acid, and (3·9 pts. = 1 equiv.) previously diluted with 2 pts. water, that is to say, he considers 1 eq. or ½ mol. sulphuric acid sufficient to expel the acetic acid from 1 mol. sodium acetate. The dilution of the sulphuric acid with half its weight of water is found, however, to yield much better results than the use of the undiluted acid. An increase of the quantity of sulphuric acid to 1½ or 1¾ equiv. does neither good nor harm if the acid be diluted with water as just stated; if, however, the acid is to be used without dilution, it is better to use a larger quantity, in order to avoid the high temperature and consequent liability to decomposition attending the use of the smaller proportion.

Solidifying Temperatures of Aqueous Acetic Acid.—Grimaux (*Compt. rend.* lxxvi. 486) has determined the crystallising points of mixtures of glacial acetic acid and water, with results differing considerably from those of Rüdorff (*2nd Suppl.* 5). The numbers in the first and second columns of the following table indicate the proportions of glacial acetic acid and water by weight.

Water.	Acetic acid.	Temp. observed, mean.	Water.	Acetic acid.	Temp. observed, mean.
7·31	92·69	+ 5·4°	49·38	50·62	- 19·8°
13·25	86·75	- 1·4	56·54	43·46	16·4
23·52	76·48	• 11·7	61·68	38·22	14·5
31·18	68·82	19·0	69·23	30·77	10·9
33·56	66·44	20·6	76·23	23·77	8·2
38·14	61·86	24·1	79·22	20·78	7·2
44·50	55·50	22·3	81·89	18·11	6·3

From this table it would appear that the lowest freezing temperature (-24·1°) answers to a mixture containing 37 or 38 per cent. water, that is to an acid represented by the formula $\text{C}^2\text{H}^4\text{O}^2 \cdot 2\text{H}^2\text{O}$. According to Rüdorff, on the other hand, the lowest freezing temperature of the aqueous acid is +0·2°, and answers to a mixture containing 13·04 per cent. water.

Estimation and Separation.—In the volumetric estimation of acetic acid and its salts in presence of mineral acids, G. Witz (*Dingl. polyt. J.* cxxiv. 312) recommends the use of methylaniline-violet as a colour-test in place of litmus, because it is not affected by acetic acid. Mineral acids, even in very small quantity, change the violet to a bluish green. The violet will therefore show at once whether a sample of vinegar, for example, contains even a trace of mineral acid; and the amount both of the mineral acid and of the acetic acid may be determined by means of a standard solution

of acetic acid may be determined by difference. With this test also the acetic acid in acetates may be readily estimated by means of a standard mineral acid solution, the change of colour in the violet not taking place till the basic constituent is neutralised and a slight excess of mineral acid is left free. Free acetic acid, if present, may be easily estimated in the usual manner by means of litmus; solutions containing only 1000 parts of sodium acetate are rather beyond the limits of this method; but it is sufficiently accurate with solutions containing 100 of that salt, and in a case of greater concentration is quite satisfactory.

In estimating the acetic acid in lead acetate by this method, it is best to precipitate the lead with sodium sulphate, as its presence in the solution interferes with the delicacy of the reaction. It is not necessary to filter the liquid, but a little more of the violet must be added than would otherwise be needed.

For the separation of acetic from propionic acid by conversion into lead salts, see *2nd Suppl.* 1010.

Mutual Displacement of Acetic and Formic Acids.—When a mixture of acetic and sodium formate is distilled, a very considerable quantity of formic acid is found in the

distillate, but even with a large excess of acetic acid complete decomposition of the formate was never obtained.

Most of the formates which are soluble in acetic acid are decomposable in like manner, some indeed without even the application of heat; thus, potassium formate dissolves in acetic acid, and if allowed to evaporate spontaneously, gives a residue consisting mainly of potassium acetate. There would appear, therefore, to be an equilibrium established between the quantity of formic acid set at liberty, and of acetate produced.

When one part of sodium formate is dissolved with heat in five parts of monohydrated acetic acid, crystals are obtained on cooling, which have the composition $\text{NaC}^2\text{H}^3\text{O}^2 \cdot 2\text{C}^2\text{H}^3\text{O}^2 + \text{NaCHO}^2 \cdot 2\text{CH}^3\text{O}^2$ (Lescaeur, *Bull. Soc. Chim.* [2], xxiii. 259).

Molecular Compound of Acetic Acid with Bromine and Hydrobromic Acid.—The mixture of bromine, acetic acid, and hydrobromic acid formed in the preparation of bromoacetic acid was observed by Steiner (*Deuts. Chem. Ges. Ber.* vii. 184) to solidify at a low temperature to a mass of crystals having the composition $(\text{C}^2\text{H}^3\text{O}^2)^2 \cdot \text{Br}^2 \cdot \frac{1}{2}\text{HBr}$. The same compound may also be readily formed by saturating acetic acid with hydrobromic and dry hydrogen bromide, then cooling the liquid and adding bromine. The crystals, after draining on a porous tile, melt, with decomposition, at 8° . They are also decomposed by water, and yield bromoacetic acid when heated in sealed tubes.

Metallic Acetates. Ammonium Acetate.—Commercial ammonium acetate is an acid salt, and if it has been prepared by heat it also contains acetamide. It may be obtained pure by evaporating the solution of the commercial salt with an excess of ammonia, completing the evaporation at a low temperature. It must then be left to cool in ammonia gas, broken up, and left for several months under a bell-jar filled with ammonia gas. The salt thus prepared has no acid reaction; it crystallises in long needles resembling potassium nitrate, and dissolving in water with rise of temperature. In this respect it resembles the acetates of potassium and sodium, which may also be obtained anhydrous by drying them at the ordinary temperature, and likewise evolve heat in dissolving (Berthelot, *Bull. Soc. Chim.* [2], xxii. 440).

When commercial ammonium acetate is dissolved in its own weight of crystallisable acetic acid, an acid ammonium acetate is obtained which crystallises in long brilliant needles, having the composition $3\text{C}^2\text{H}^3\text{O}^2 \cdot 2(\text{NH}^4\text{C}^2\text{H}^3\text{O}^2) \cdot \text{H}^2\text{O}$ (Berthelot, *ibid.* xxiv. 107).

Sodium Acetate.—Reischauer (*Chem. Cent.* 1860, 875) found that crystallised sodium acetate, $\text{C}^2\text{H}^3\text{NaO}^2 + 6\text{H}^2\text{O}$, loses the whole of its water in a vacuum at the ordinary temperature, and that in this state it may be fused without sensible loss of weight. The fused salt, if exposed to a damp atmosphere, quickly takes up about 14 mols. of water, forming a supersaturated solution; whereas the unfused salt takes up from the air only the original 6 mols. water, without any essential alteration of appearance. The supersaturated solution, if quickly brought in contact with hard bodies, solidifies, with great rise of temperature, to a moist crystalline mass, which on simple desiccation gives up only the quantity of water (8 mols.) which is in excess of the 6 mols. of the ordinary crystallised salt stable at ordinary temperatures.

The thermic relations accompanying these changes have been investigated by Berthelot (*Bull. Soc. Chim.* [2], xxi. 60), with the following results:—

	Heat evolved.
(1) Vacuum-dried salt dissolved in 50 parts of water at 7°	+ 4.08 kil.-degrees
(2) Fused dried salt dissolved in 50 parts of water at 7°	+ 3.23 "
Heat evolved by action of hydrochloric acid (1 centigram to 2 litres) on solution (1)	+ 0.86 "
Heat evolved by action of hydrochloric acid (1 centigram to 2 litres) on solution (2)	+ 0.85 "
Heat evolved by action of hydrochloric acid (1 centigram to 2 litres) on solution of hexhydrated salt	+ 0.85 "

Potassium acetate likewise gives off all its water in a vacuum.

The vacuum-dried salt dissolved in water evolves	+ 3.27 kil.-degrees
The fused salt	+ 3.21 "

From these results it appears that the anhydrous acetates of the alkali metals are the same, in whatever way the dehydration may have been effected; also that the solutions of the anhydrous and hydrated salts are identical. Reischauer's results may perhaps be explained on the supposition that the dehydration of the acetate in a

vacuum takes place rather slowly, and that the smallest quantity of hydrated salt is sufficient to prevent the formation of a supersaturated solution. At all events this solution may be supposed to contain either the anhydrous salt or a hydrate with less than 6 mols. water. Moreover, since by addition of water to this solution a dilute solution is formed without any considerable alteration of temperature, and since the addition of the crystallised hydrate to a solution supersaturated, but diluted with so much water that nothing is separated from it by contact with the crystals does not give rise to any peculiar thermic action, it is probable that even dilute solutions still contain anhydrous salt mixed with a quantity of the hydrated salt, perhaps increasing with the dilution. It is the sudden formation of the solid hydrate in the crystalline state and through the entire solution that destroys the state of supersaturation, just as in sodium sulphate and other salts.

Action of Carbonic Acid on Sodium Acetate.—A saturated solution of sodium acetate is decomposed by carbonic acid at the temperature of a mixture of snow and salt, with formation of acid carbonate, NaHCO_3 , and free acetic acid (Setchenow, *Deut. Chem. Ges. Ber.* viii. 540).

Alcoholic Acetates. Acetic Ethers.—Paterno finds that in the preparation of ethyl acetate (also of ethyl iodide), it is not advisable to use perfectly anhydrous materials, a better yield being obtained when a little water is present (*Gazz. Chim. Ital.* iv. 149). According to Schiff (*Deut. Chem. Ges. Ber.* vii. 592), the same observation is applicable in etherifications in general.

Action of Bromine on Acetic Ethers.—When methyl acetate is heated to 150° with 5 at. bromine, hydrobromic acid and methyl bromide are produced, together with a laminar crystalline substance having the composition of hex brominated methyl acetate, $\text{C}^6\text{H}^3\text{Br}^3\text{O}^2$. This compound melts at 86° – 87° , crystallises from alcohol in needles, emits a vapour which attacks the eyes, and is easily decomposed by fixed alkalis and by alcoholic ammonia, a humus-like substance being formed in the latter case. The action of bromine on methyl acetate likewise gives rise to a small quantity of bromoacform, which is decomposed by alcoholic ammonia, with production of dibromacetamide and bromoform.

Ethyl acetate, treated with 2 mols. bromine at 150° – 160° , is for the most part converted into ethyl bromide and dibromoacetic acid, together with small quantities of brominated ethyl bromides and pentabrominated ethyl acetate, $\text{C}^5\text{H}^2\text{Br}^5\text{O}^2$. This latter product forms a colourless oil having an ethereal odour, and boiling with decomposition above 200° . Alcoholic ammonia converts it into dibromacetamide (m. p. 156°), ammonium bromide, and a syrupy substance.

The action of bromine on ethyl acetate probably consists, in the first instance, in the formation of brominated derivatives of ethyl bromide, which are afterwards decomposed by the hydrobromic acid simultaneously produced (A. Steiner, *Deut. Chem. Ges. Ber.* vii. 404).

When bromine is mixed with ethyl acetate at ordinary temperatures, heat is evolved, the product retains the colour of bromine, and does not crystallise by cooling; and when distilled under reduced pressure gives off at 40° – 45° a liquid having the composition $(\text{C}^2\text{H}^3\text{O}^2)^2\text{Br}^2$. On the other hand, when a stream of dry air is passed through a mixture of ethyl acetate and bromine in any proportions, the excess of one or the other is carried away till the residue has the composition $\text{C}^4\text{H}^4\text{O}^4\text{Br}^2$. This compound decomposes at 140° – 150° , yielding ethyl bromide, hydrogen bromide, and bromoacetic acid (Schützenberger, *Bull. Soc. Chim.* [2], xix. 47).

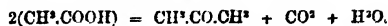
Decomposition of Ethyl Acetate by Heat.—When the vapour of this ether is passed through an iron tube heated to a temperature somewhat below dull redness, it is resolved into acetic acid and ethane:



If, however, the heat be raised to dull redness, the acetic acid is further resolved into acetone, carbon dioxide, and methane:



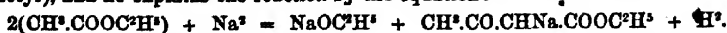
and



Acetoacetic Ethers and their derivatives.—The products obtained by the successive action of sodium and alcoholic iodides, chlorides, &c., on ethyl acetate (1st *Suppl.* 15, 689), have been further examined by Wislicenus and his pupils (*Deut. Chem. Ges. Ber.* vii. 663, viii. 1034, 1200; *Liebigs Annalen*, clxxvi. 161), and by Oppenheim & Precht (*Deut. Chem. Ges. Ber.* vii. 929; ix. 318).

1. Wislicenus finds, in accordance with Geuther, that the only products formed by the direct action of sodium on ethyl acetate, are sodium ethylate, $\text{C}^2\text{H}^5\text{NaO}$, and ethyl

acetosodacetate, $C^2H^3NaO^2$ (Geuther's sodium ethyldiacetate; Wanklyn's sodium-triacetyl), and he explains the reaction by the equation:



Oppenheim a. Precht, in accordance with Wanklyn (1st Suppl. 15), explain the result by the action of 4 at. sodium on 3 mols. acetic ether:—



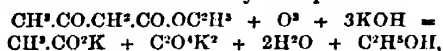
According to this equation, 4 at. = 92 parts of sodium should form 1 mol. = 130 parts by weight of acetosodacetic ether, or 1 part of sodium should form 1.41 parts of the ether. In four experiments 1 part of sodium gave 1.5 parts of the ether.

The action of sodium on acetic ether generally begins in the cold, with evolution of hydrogen; but, if the ether be previously treated with phosphoric anhydride, which removes alcohol as well as water, and then distilled, perfectly pure ethyl acetate passes over, which is but slowly attacked by sodium even at the heat of the water-bath, and without evolution of hydrogen. This result is in accordance with the observations of Wanklyn and of Ladenburg, who purifies his acetic ether with silicic chloride (2nd Suppl. 7), also with the original experiments of Löwig a. Weidmann, made in 1840.

2. *Ethylic Aceto-acetate*, $C^2H^4O^2 = CH^3-CO-CH^2-CO^2C^2H^3$ (Geuther's *Ethyl-diacetic acid*, Wanklyn's *Hydrogen-triacetyl* or *Acetate of acetethyl*). To prepare this compound in the pure state, Oppenheim a. Precht adopt a method differing but slightly from that originally given by Geuther (1st Suppl. 16). The product obtained by heating sodium with excess of ethyl acetate—while still warm, and therefore dissolved in the acetic ether, and without purification by washing with ether or solution in water—is mixed with the quantity of glacial acetic acid required to convert it into the aceto-acetic ether, and then with water; or, better: The weighed quantity of glacial acetic acid is mixed with four times its weight of water, and the product obtained by treating 1 part of sodium with 10 parts of ethyl acetate (i.e. with a large excess) is poured while still warm into the acid liquid. The mixture of acetic and aceto-acetic ether thus produced floats on the solution of sodium acetate formed at the same time, and is decanted therefrom and subjected to fractional distillation. In this manner 2 kilograms of pure aceto-acetic ether, boiling at $180^\circ-181^\circ$, may be prepared in a few days.

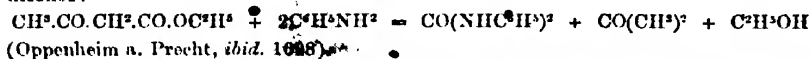
Mixter (*Deut. Chem. Ges. Ber.* vii. 522) prepares the same ether by the action of acetyl chloride on the product obtained by heating ethyl acetate with sodium. In this case the acetyl chloride first acts on the acetosodacetic ether, $CH^3.CO.CHNa.CO^2C^2H^3$, replacing its sodium by acetyl, and the product thus formed is subsequently decomposed by water into acetic acid and ethyl aceto-acetate.

Ethylic aceto-acetate gently warmed with a dilute solution of potassium permanganate is oxidised in the manner indicated by the equation:

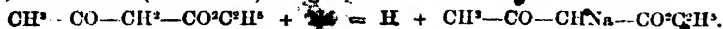


the only acids formed being acetic and oxalic (Emmerling a. Oppenheim, *Deut. Chem. Ges. Ber.* ix. 1008).

Ethylic aceto-acetate, heated with aniline, yields diphenyl-carbamide, acetone, and alcohol:

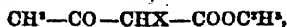


3. Ethylic aceto-acetate forms the starting point of a large number of derivatives. Sodium dissolves in it with evolution of hydrogen, and if the liquid be diluted with anhydrous ether, or better with pure benzene (3 mols. benzene to 1 vol. of the aceto-acetic ether), the reaction goes on with great regularity at the boiling point of benzene, 1 at. sodium (never more) being introduced into 1 mol. of the ether:—



It is best to use an excess of sodium, and decant the liquid as soon as hydrogen ceases to escape. The acetosodacetic ether thus produced crystallises out on cooling, and remains, after evaporation of the benzene, as a snow-white mass having a silky lustre.

By treating this compound with the iodides, bromides, &c., of organic radicles, the atom of sodium may be replaced in perfectly definite proportion, yielding compounds having the general formula:

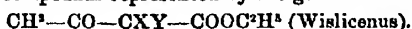


where X denotes a univalent organic radicle, or the equivalent quantity of a multi-valent radicle. Thus by treating 75 grams of ethylic aceto-acetate with sodium, and the

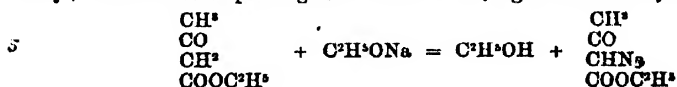
resulting ethyl aceto-sodacetate with ethyl iodide, Wislicenus obtained, after three fractional distillations, 56 grams of pure ethylic acetethylacetate, $\text{CH}_3\text{—CO—CH}(\text{C}^2\text{H}_5)\text{—COOC}^2\text{H}_5$, boiling between 193° and 195° , the only other product being a small quantity of dehydracetic acid. Equally definite are the reactions with benzyl chloride, benzoyl chloride, ethyl chloracetate, &c.

In the products of this first synthesis—but not before—a second atom of hydrogen may be replaced by sodium. Ethylic aceto-acetate diluted with benzene dissolves exactly 1 atom of sodium—never more—yielding ethylic acetosodethylacetate, $\text{CH}_3\text{.CO.C}(\text{C}^2\text{H}_5)\text{Na.COOC}^2\text{H}_5$; which again reacts in a similar manner with organic haloids, yielding with ethyl bromide, for example, a comparatively large quantity of ethylic aceto-diethylacetate, $\text{CH}_3\text{.CO.C}(\text{C}^2\text{H}_5)_2\text{.COOC}^2\text{H}_5$, boiling at $208^\circ\text{—}211^\circ$. The secondary products were of insignificant amount, including a small quantity of dehydracetic acid.

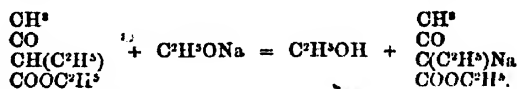
In a similar manner two different organic radicles may be introduced into the molecule, producing compounds represented by the general formula:



4. To explain the formation of ethylic aceto-diethylacetate by the action of ethyl iodide on a mixture of ethylic aceto-sodacetate and sodium ethylate, in Frankland & Dappa's synthesis, Geuther suggested that the ethyl of the sodium ethylate, in presence of ethylic acetate, replaces the atom of hydrogen in the ethylic aceto-ethylacetate. Wislicenus, however, shows by experiment that this is not the case, but that sodium ethylate acting upon the aceto-acetate or aceto-ethylacetate of ethyl, forms the corresponding sodium-derivative, together with ethyl alcohol, thus:—



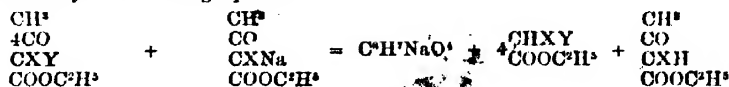
and,



An experiment with 40 grams of pure ethyl aceto-acetate and 22 grams of pure and dry sodium ethylate gave 14.4 grams of ethyl alcohol, the calculated quantity being 14.1 grams.

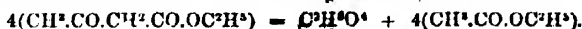
From the facility with which these transformations occur, it is easy to see that in the action of ethyl iodide on the crude product obtained by treating ethyl acetate with sodium, the reaction between the ethylic aceto-ethylacetate formed in the first instance, and the sodium ethylate still present in the mixture, must give rise, first to ethyl acetethylsodacetate, and then to ethylic acetodiethylacetate (Wislicenus).

5. The resolution of the ketonic acids into homologues of acetic acid and other products, among which dehydracetic acid, $\text{C}^2\text{H}^2\text{O}^2$, is invariably found, is attributed by Wislicenus to a reaction between the sodic and non-sodic aceto-acetic ethers, as represented by the following equation:



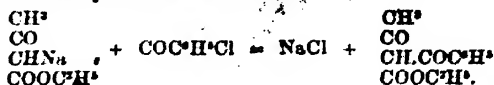
where X Y denote either organic radicles or hydrogen-atoms (Wislicenus).

6. *Ethylic aceto-acetate*, heated in a sealed tube to $230^\circ\text{—}250^\circ$, is decomposed into ethyl acetate and dehydracetic acid, as represented by the equation:

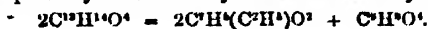


Ethylic aceto-ethylacetate remains unaltered up to 300° , but is decomposed at 300° in the same manner as the aceto-acetate (Conrad, *Dout. Chem. Ges. Ber.* vii. 688).

7. *Ethylic Benzoyl-aceto-acetate*, $\text{C}^6\text{H}_5\text{O}^2$, is formed by the action of benzoyl chloride on ethylic acetosodacetate:



This ether is decomposed by heat into ethyl benzoate and dehydracetic acid:

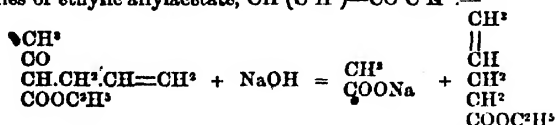


Treated with alcoholic potash, it does not yield the double ketone $\begin{array}{c} \text{CO} \cdot \text{CH}^1 \\ | \\ \text{CH}^2 \text{CO} \cdot \text{C}^3 \text{H}^3 \end{array}$ as

might be expected, according to its constitution, inasmuch as this ether is itself decomposed by the potash, giving potassium acetate and phenyl-methyl ketone, together with small quantities of potassium benzoate and acetone (J. Bonné, *Deut. Chem. Ges. Ber.* vii. 689).

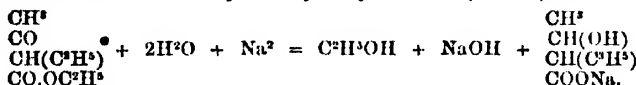
8. *Ethyllic Allyl-aceto-acetate* = $\text{CH}^3 \cdot \text{CO} \cdot \text{CH}(\text{CH}^2 \cdot \text{CH} = \text{CH}^2) \cdot \text{CH}^2 \cdot \text{CO} \cdot \text{C}^3 \text{H}^3$, is formed by the action of allyl iodide on ethylic acetosodacetate. This ether boiled with alcoholic potash is easily resolved into alcohol, carbonic acid, and amyl-acetone or methyl-crotonyl ketone, $\text{CH}^3 - \text{CO} - \text{CH}^2(\text{CH}^2 - \text{CH} = \text{CH}^2)$, a light colourless oil boiling at 130° .

Ethylic allyl-aceto-acetate heated with pure sodium ethylate (? hydrate) yields large quantities of ethylic allylacetate, $\text{CH}^2(\text{C}^3 \text{H}^3) - \text{CO} \cdot \text{C}^2 \text{H}^5$:—



a liquid boiling at $142^\circ - 144^\circ$, from which allyl-acetic acid, $\text{CH}^2(\text{C}^3 \text{H}^3) - \text{COOH}$, may be obtained in the usual way (Zeidler, *ibid.* viii. 1035).

Ethylic allyl-aceto-acetate, dissolved in aqueous alcohol and treated with sodium amalgam, is converted into a-allyl- β -oxybutyric acid (Zeidler):—



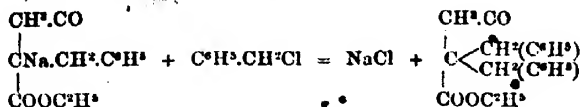
Isobutylic Aceto-acetate, $\text{C}^4 \text{H}^{10} \text{O}^2 = \text{CH}^3 - \text{CO} - \text{CH}^2 - \text{CO}^2[\text{CH}^2 \cdot \text{CH}(\text{CH}^3)^2]$, is prepared by treating the product of the action of sodium on isobutyl acetate with glacial acetic acid, in the manner above described for the preparation of ethyl aceto-acetate (p. 12). It is a colourless liquid which smells faintly of fœnel, has a sp. gr. of 0.979 at 0° , and 0.922 at 23° , and boils with decomposition at 203° . It dissolves sodium rapidly, and on mixing the solution with sodium isobutylate, $\text{C}^4 \text{H}^9 \text{ONa}$, and chloroform, boiling the mixture with caustic soda, and adding hydrochloric acid, yellowish flocks are thrown down consisting of oxyacetic acid, $\text{C}^2 \text{H}^{10} \text{O}^2$ (p. 17) (Emmerling a. Oppenheim, *Deut. Chem. Ges. Ber.* ix. 1096).

10. *Ethyl Acetodi-isobutylacetate*, $\text{C}^4 \text{H}^{10} \text{O}^3 = \text{CH}^3 \cdot \text{CO} \cdot \text{C}(\text{C}^4 \text{H}^9)^2 \cdot \text{CO} \cdot \text{OC}^2 \text{H}^5$.—This ether is prepared by the action of isobutyl iodide, first at ordinary temperature, afterwards at the heat of the water-bath, on the product of the action of sodium on acetic ether, and is separated from the crude product (boiling at $130^\circ - 260^\circ$) by repeated fractionation. It is a liquid of agreeable odour, having a sp. gr. of 0.947 at 10° , and boiling at $250^\circ - 253^\circ$. It dissolves in all proportions in alcohol and ether, and forms with fuming sulphuric acid, a sulpho-acid which yields an uncrystallisable barium salt.

The lower-boiling portions of the crude product appear to contain ethylic aceto-monobutylacetate. When the portion boiling between 200° and 210° is boiled with baryta-water, large quantities of barium carbonate are deposited, and the mixture, distilled in a current of steam, yields a liquid, smelling like amyl acetate, boiling at $144^\circ - 146^\circ$, insoluble in water, on which it floats, but soluble in alcohol and ether, forming solutions which are neutral to vegetable colours. This liquid has the composition $\text{C}^4 \text{H}^{10} \text{O}$, and may be regarded as isobutyl acetone or methyl-isopentyl ketone, $\text{CH}^3 - \text{CO} - \text{CH}^2(\text{C}^4 \text{H}^9)$, (Mixer, *Deut. Chem. Ges. Ber.* vii. 499).

11. *Ethyllic Benzyl-aceto-acetate*, $\text{C}^{13} \text{H}^{18} \text{O}^3 = \text{CH}^3 \cdot \text{CO} \cdot \text{CH}(\text{CH}^2 \cdot \text{C}^6 \text{H}^5) \cdot \text{CO} \cdot \text{C}^2 \text{H}^5$, is formed by the action of benzyl chloride on ethyl sodacetate. When decomposed by an alkali it yields methyl-phenyl-ethyl ketone, $\text{CH}^3 - \text{CO} - \text{C}^2 \text{H}^4(\text{C}^6 \text{H}^5)$, a liquid boiling at 233° (Ehrlich, *ibid.* 690).

The same ether takes up an atom of sodium, forming ethylic sodio-benzyl aceto-acetate, and this is converted by benzyl chloride into ethylic dibenzyl-aceto-acetate:—



This last ether is a viscid oil, not distillable without alteration.

Ethyllic benzyl-acetate is converted by nascent hydrogen evolved from sodium amalgam into α -benzyl- β -oxybutyric acid, $\text{CH}_3\text{CH(OH).CH(C}_6\text{H}_5\text{).COOH}$ (Ehrlich, *ibid.* 1036).

12. *Ethyllic Methylaceto-acetate* (b.p. 185° – 186°), formed by the action of methyl iodide on ethyl sodaceto-acetate, is converted by sodium amalgam into α -methyl- β -oxybutyric acid (Rohrbeck, *ibid.* 1036); ethylic ethylaceto-acetate in like manner into the corresponding ethyloxybutyric acid, $\text{CH}_3\text{—CHOH—CH(C}_6\text{H}_5\text{)—COOH}$ (Wajdschmidt).

13. *Ethyllic Methyl-ethylaceto-acetate*, $\text{CH}_3\text{CO.C(CH}_3\text{)(C}_6\text{H}_5\text{).COOC}_2\text{H}_5$, formed by the action of methyl iodide on ethylic sodethylaceto-acetate, is a colourless mobile oil boiling at 198° . Distilled with dry sodium ethylate, it yields ethylic methyl-ethylacetate, $\text{CH}_3\text{CH}_2\text{CH(COOC}_2\text{H}_5\text{)COOC}_2\text{H}_5$, an oil boiling at 132° , which yields,

by the usual method, methyl-ethyl-acetic acid, $\text{C}_6\text{H}_5\text{H}_2\text{O}_2 = \text{CH}_3\text{CH}_2\text{CH(COOH)COOH}$, boiling at 173° , and resembling optically active valeric acid, in every respect excepting that its barium salt is uncrystallisable (Saur, *ibid.* 1037).

14. *Ethyllic aceto-acetate* saturated at ordinary temperatures with dry chlorine, is converted into ethylic acetodichloracetate, $\text{C}_6\text{H}_5\text{CHCl}_2\text{COOC}_2\text{H}_5$, a colourless oil, which boils at 205° – 207° , is resolved by heating with water to 120° into alcohol, carbon dioxide, and dichloroacetone, $\text{CH}_3\text{CO.CHCl}_2$, boiling at 120° , and by saponification chiefly into acetate and dichloracetate. Both these reactions show that ethylic acetodichloracetate has its two chlorine-atoms united with the same carbon atom, but leave it undecided whether its constitution should be represented by the formula: $\text{CHCl}_2\text{—CO—CH}_2\text{—COOC}_2\text{H}_5$, or by $\text{CH}_3\text{—CO—CCl}_2\text{—COOC}_2\text{H}_5$.

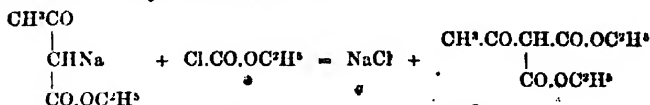
Ethylic ethylaceto-acetate, treated in like manner, takes up only 1 atom of chlorine. Hence there can be but little doubt that ethylic ethylacetochloracetate, boiling between 215° and 220° , has the formula $\text{CH}_3\text{CO.CCl.C}_6\text{H}_5\text{COOC}_2\text{H}_5$, which moreover leads to the second of the above formulae for ethylic acetodichloracetate.

Ethylic ethylacetochloracetate, heated with water to 180° , is resolved into alcohol, carbon dioxide, and methyl-chloropropyl ketone (b. p. 130°):



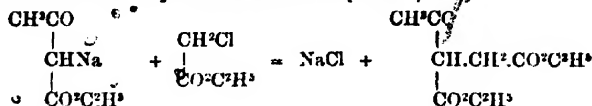
(Conrad, *ibid.* 1038).

15. *Diethyllic Acetomalonate*, $\text{C}_6\text{H}_5\text{H}_2\text{O}_4$, is formed by the action of ethylic chloro-carbonate on ethylic acetosodacetate:

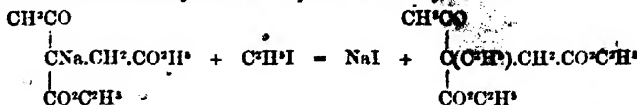


It is a colourless oil, of sp. gr. 1.080 at 23° , boiling at 238° – 240° .

16. *Diethyllic Acetosuccinate*, $\text{C}_6\text{H}_5\text{H}_2\text{O}_4$, is produced by the action of ethyl monochloracetate on ethylic acetosodacetate (Conrad):

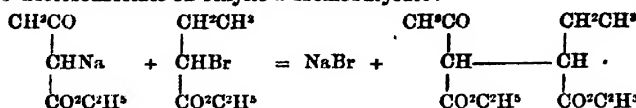


17. *Diethyllic α -Ethyl-acetosuccinate*, $\text{C}_6\text{H}_5\text{H}_2\text{O}_4$, is formed by treating the sodium derivative of diethyllic acetosuccinate with ethyl iodide:



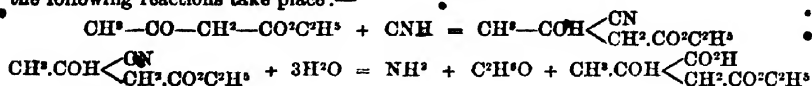
It boils at 263° – 265° and does not dissolve sodium, either at ordinary temperatures or when gently heated (Huggenberg, *Deut. Chem. Ges. Ber.* viii. 1209).

18. *Diethyl β-Ethyl-acetosuccinate*, $C^{12}H^{20}O^5$, is obtained by the action of ethylic acetosodacetate on ethylic α-bromobutyrate:



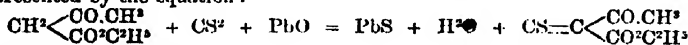
It is a colourless oil which boils at 262° , and dissolves sodium, with evolution of hydrogen, at ordinary temperatures (Clowes, *ibid.* 1208).

19. When ethylic aceto-acetate is heated to 100° for three hours with half its weight of anhydrous *prussic acid*, and the product is afterwards heated with hydrochloric acid, the following reactions take place:—



The product is a modification of oxyprotyrotartaric acid, which has not been obtained in the crystalline form (Demarçay, *Compt. rend.* lxxii. 1337). (See OXYPROTYROTARTARIC ACID.)

20. *Action of CS^2 and Metallic Oxides on Ethylic Aceto-acetate.*—When this ether is heated to 100° in a sealed tube with carbon sulphide and lead oxide or zinc oxide, a small quantity of carbon oxy-sulphide is formed, together with a hard mass mostly consisting of lead or zinc sulphide, from which boiling alcohol extracts a product crystallising in small woolly straw-yellow needles, melting at 156° – 162° , and giving by analysis numbers agreeing with the formula $C^4H^4SO^2$. This substance is the ethylic ether of thiocarbaceto-acetic acid, $\text{CS}=\text{C} \begin{array}{l} \text{CO} \cdot \text{CH}^3 \\ \text{CO}^2\text{H} \end{array}$, and its formation may be represented by the equation:



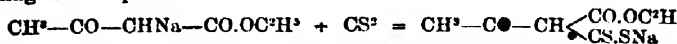
Ethylic Aceto-acetate.

Ethylic Thiocarbaceto-acetate.

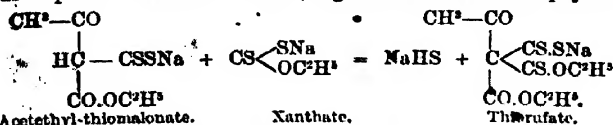
The acid $\text{CS}=\text{CH}-\text{CO}^2\text{H}$ (thiocarbacetic acid) of which thiocarbaceto-acetic acid is the acetylated derivative, has not yet been obtained (Norton a. Oppenheim, *Deut. Chem. Ges. Ber.* x. 701).

21. *Action of Carbon Disulphide on Ethylic Sodacetate.*—The crude product of the action of sodium on acetic ether is readily attacked at a gentle heat by carbon disulphide, yielding a solid dark brown product, and a solution containing the products of decomposition of sodium xanthate, together with sodium sulphide. On filtering off the liquid and washing the residue with water, a light red sodium salt is obtained having the composition $C^{10}H^{12}S^2O^4Na$, and yielding, by double decomposition with calcium chloride, a calcium salt, $(C^{10}H^{12}S^2O^4)^2Ca$. With mercuric chloride, lead nitrate and a strong solution of zinc sulphate, the sodium salt gives orange-coloured precipitates; with iron salts a brown; with silver nitrate a dark red precipitate, soon turning brown; and with copper sulphate, a black precipitate.

The acid $C^{10}H^{12}S^2O^4$ (thiorufic acid) precipitated by hydrochloric acid and from the sodium salt, forms dark orange-coloured nacreous scales very much like azobenzene, nearly insoluble in water, very soluble in alcohol and acetic acid, and decomposing readily when the solutions are evaporated. The formation of thiorufic acid appears to take place by two stages: 1. The action of CS^2 on the ethylic sodacetate gives rise to the sodium salt of acetylated ethyl-thiomalonie acid, $\text{CH}^3-\text{CO}-\text{CH} \begin{array}{l} \text{CO} \cdot \text{OC}^2\text{H}^5 \\ \text{CS} \cdot \text{SNa} \end{array}$; according to the equation:



and this salt reacts with the sodium xanthate formed at the same time in such a manner as to produce sodium thiorufate, together with sodium sulphhydrate:—



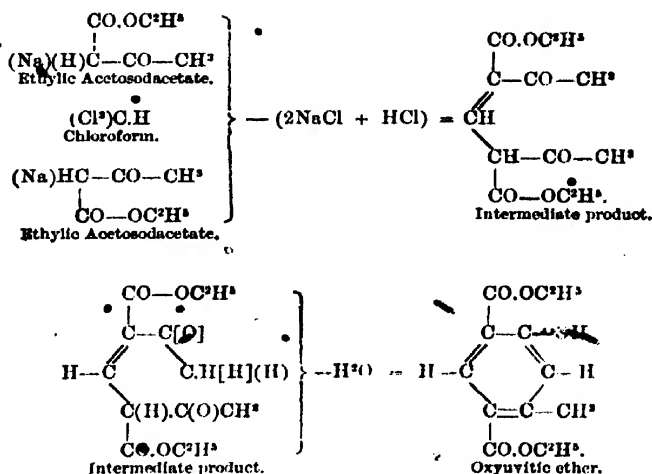
On boiling the thiorufate with soda-ley in a vessel fitted with a reversed condenser, the salt acquires a transient red colour, and large quantities of alcohol are produced,

together with the salt of a new orange-red acid very soluble in water (Norton a. Oppenheim, *loc. cit.*)

22. *Action of Chloroform on Sodacetic Ether.*—When chloroform is added to pure ethylic acetosodacetate, brisk tumefaction and ebullition takes place; but on distilling the liquid, nothing passes over except acetic ether and tribasic formic ether. When, however, chloroform is added to the crude product of the action of sodium on acetic ether, and the resulting mixture of ether is boiled with caustic soda, till a sample of it no longer yields an oily product on addition of an acid, a solution is obtained from which hydrochloric acid throws down oxyvitic acid,

$\text{C}^{\text{H}}\text{H}^{\text{O}}\text{O}^{\text{H}} = \text{C}^{\text{H}}\text{H}^{\text{O}}\text{H}^{\text{O}} \left\{ \begin{array}{l} \text{CH}^{\text{O}} \\ \text{OH} \\ (\text{CO}^{\text{O}}\text{H})^{\text{O}} \end{array} \right.$, in yellowish flocks, which may be dissolved in a large quantity of boiling water, and decolorised by animal charcoal, the acid then separating on cooling, in thin colourless needles.

This acid results from the action of 1 mol. chloroform on 2 mols. ethylic sodacetate. :—



(Oppenheim a. Pfaff, *Deut. Chem. Ges. Ber.* vii. 929.)

As already observed, however, the oxyvitic acid is not produced from chloroform and ethylic acetosodacetate alone; its formation requires the intervention of sodium ethylate, which, in fact, is present in the crude product of the action of sodium on acetic ether. Moreover, the addition of sodium ethylate to the mixture of chloroform and pure ethylic acetosodacetate at once determines the formation of the oxyvitic acid.

As the bibasic oxyvitic acid is formed at the expense of 1 mol. chloroform and 2 mols. ethylic acetosodacetate, the sodium ethylate appears to get by introducing into the residue of 1 mol. acetosodacetic ether remaining after the partial action of the chloroform a second atom of sodium, whereby the third chlorine-atom of the chloroform can be separated.

That the ethyl-group in the sodacetic ether is not directly concerned in the formation of the oxyvitic acid is shown by the fact that this acid, and not a higher homologue, is formed in like manner from isobutyl acetate (Emmerling a. Oppenheim, p. 14).

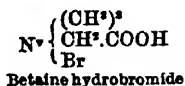
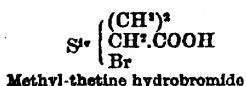
Oxyvitic acid belongs to the aromatic group, and accordingly gives a red coloration with ferric chloride; its formation affords, therefore, an example of the passage from the fatty to the aromatic group.

The product obtained by treating pure ethylic acetosodacetate with chloroform alone gives no colour reaction with ferric chloride, and therefore does not belong to the aromatic group. It appears to be a tribasic acid resulting from the action of 3 mols. chloroform on 1 mol. acetosodacetic ether (Oppenheim a. Precht, *Deut. Chem. Ges. Ber.* ix. 321).

Aromatic Acids.—*Monobromacetic acid* unites with methyl sulphide, forming the compound $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{S.C}^{\text{H}}\text{H}^{\text{O}}\text{BrO}^{\text{H}}$, which may be formulated as the hydro-
3rd. Svp.

9017.

bromide of a base, $C^4H^5SO^2$, called *methyl-thetine*, analogous in constitution to betaine, $C^4H^5NO^2$.—



The constitution of the so-called methyl-thetine is similar to that of the sulphine-compounds discovered by v. Oeffele (v. 881); Drum-Brown & Letts, *Deut. Chem. Ges. Ber.* vii. 695).

Dibromacetic acid, $C^2H^2Br^2O^2 = CHBr^2.COOH$.—L. Schäffer (*Deut. Chem. Ges. Ber.* iv. 366) has separated this acid from the bye-products of the manufacture of bromal. The portion of the crude product which boils above 180° was mixed with water; the aqueous solution decanted from the carbon tetrabromide which separates, then neutralised with barium carbonate; and the crude barium dibromacetate thus obtained was purified by treatment with animal charcoal and repeated crystallisation. From this salt the acid was separated by sulphuric acid.

Dibromacetic acid forms thick white crystalline masses, but cannot be obtained in well-defined separate crystals, as it does not solidify till the last trace of the solvent has been removed. It is easily soluble in alcohol and ether. It smells faintly of acetic acid, and its vapour strongly irritates the mucous membranes. It boils, with slight decomposition, at 232° – 234° (according to Perkin & Duppa at 225° – 230°). The observations of its melting point vary from 45° – 50° , as the acid quickly absorbs moisture from the air. The acid, if not quite pure, does not solidify at all in a vacuum, or only after a considerable time; but, on adding strong sulphuric acid, crystallisation takes place in a few minutes.

The dibromacetates, with exception of the silver and mercurous salts, are very soluble in water and in alcohol, and crystallise well. The *potassium salt*, $2C^2HBr^2OK + H^2O$, forms large prisms permanent in the air; the *ammonium salt* white transparent prisms. The *barium salt*, $(C^2HBr^2O^2)^2Ba + 4H^2O$, forms large shining colourless prisms, which effloresce very quickly on exposure to the air. The *lead salt*, $(C^2HBr^2O^2)^2Pb$, crystallises in stellate groups of small white shining needles. The *silver salt*, $C^2HBr^2O^2Ag$, forms small white needle-shaped crystals, which blacken when exposed to light. It detonates when heated, with formation of silver bromide, decomposes gradually by keeping, and is decomposed by water, with separation of silver bromide. The *mercurous salt* crystallises in small white shining laminae, which behave like the silver salt when heated with water. The *ethylic ether* obtained by boiling an alcoholic solution of the acid mixed with sulphuric acid, is a colourless oily liquid, insoluble in water, soluble in alcohol and ether, and having a disagreeable odour recalling that of peppermint oil. It boils constantly and without decomposition at 192° . When gently heated with alcoholic ammonia, it is converted into dibromacetamide, which separates on cooling in long, brittle, shining, needle-shaped crystals melting at 156° (Schäffer; compare Perkin & Duppa, *Chem. Soc. J.* xii. 1, and this Dictionary, i. 666).

Tribromacetic acid, $C^2HBr^3O^2 = CBr^3.COOH$ (Schäffer, *loc. cit.*; Gal, *Compt. rend.* lxxvii. 786; compare 1st *Suppl.* p. 18).—This acid is most easily prepared by dissolving bromal or bromal hydrate in warm nitric acid. The reaction is complete after some hours, and if the nitric acid is not present in too great excess, the tribromacetic acid crystallises in laminae, which may be separated from the liquid and purified by recrystallisation.

Tribromacetic acid forms tabular, transparent, colourless crystals, which are permanent in the air, have a strong lustre, and, according to M. Groth's measurements, belong to the monoclinic system. Combination $\infty P + \infty P$; cleavage perfect parallel to $-P\infty$. According to approximate measurements, the angle $\infty P : \infty P = 111^\circ 11'$; $\infty P : \infty P = 109^\circ 54'$; $\infty P : -P\infty = 107^\circ 42'$.

The acid dissolves easily in water, alcohol, and ether, and may be obtained in crystals from these solutions. The vapours are pungent, and have a slight odour of acetic acid. The acid melts at 130° (Schäffer); at 135° and boils at 250° (Gal). The acid when dry may be touched with impunity; but if moist, it produces violent inflammation of the skin (Gal).

The tribromacetates, excepting the silver and mercurous salts, are easily soluble in water and in alcohol, but are decomposed in solution even at a gentle heat, into bromoform and the corresponding carbonates; e.g.



The free acid likewise splits up in the same manner when its aqueous or alcoholic solution is heated.

The *sodium salt*, $2\text{C}^2\text{Br}^2\text{O}^2\text{Na} + 5\text{H}^2\text{O}$, forms highly lustrous white laminae; the *barium salt*, $(\text{C}^2\text{Br}^2\text{O}^2)^2\text{Ba} + 3\text{H}^2\text{O}$, thin tabular shining crystals; the *copper salt*, nodular groups of small, bluish-green, needle-shaped, easily soluble crystals; the *lead salt*, $(\text{C}^2\text{Br}^2\text{O}^2)^2\text{Pb}$, stellate groups of small compact needles. The *silver salt*, $\text{C}^2\text{Br}^2\text{O}^2\text{Ag}$, forms small, laminar, very unstable crystals. The *mercurous salt* forms small laminae, and decomposes either when moist or on exposure to light (Schäffer).

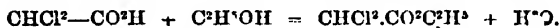
Chloracetic Acid. When dry hydrogen phosphide is passed into monochloroacetic acid, hydrochloric acid is evolved, and *chloracetyl phosphide*, $\text{C}^2\text{H}^2\text{ClOPH}^2$, is formed. This substance forms a yellowish-white powder, which in the moist state is slowly resolved into chloracetic acid and hydrogen phosphide. Its alcoholic solution, when evaporated over the water-bath, leaves a strongly acid syrup, which refuses to solidify (Steiner, *Deut. Chem. Ges. Ber.* vii. 1178).

Methyl Monochloracetate, $\text{C}^2\text{H}^2\text{ClO}^2\text{CH}^2$, may be prepared by passing hydrogen chloride into a solution of monochloroacetic acid in methyl alcohol (L. Henry, *ibid.* vii. 742), or by the action of monochloroacetyl chloride on methyl alcohol (P. J. Meyer, *ibid.* viii. 1162). It is a colourless mobile liquid having a rather pleasant odour, sp. gr. = 1.22 at 15° . Vapour-density, 3.71 (calc. 3.74). Boiling point 126° – 127° , under a pressure of 757 mm. (Henry); 129° (Meyer). It is insoluble in water, and not decomposed thereby, or very slowly if at all. It does not give off hydrogen chloride when treated with sulphuric acid. It is isomeric with methylene aceto-chloride, $\text{CH}^2\text{C}^2\text{H}^2\text{O}^2\text{Cl}$ (2nd Suppl. 80), formed by passing chlorine into cooled methyle acetate (Henry). It is converted by ammonia into chloracetamide, $\text{CH}^2\text{Cl}.\text{CONH}^2$, by aniline into chloracetanilide, $\text{CH}^2\text{Cl}.\text{CONH}(\text{C}^6\text{H}^5)$, and by toluidine into chloracetoluide, $\text{CH}^2\text{Cl}.\text{CONH}(\text{C}^6\text{H}^4)$, (Meyer).

Ethyl Dichloracetate, $\text{CHCl}^2.\text{CO}^2\text{C}^2\text{H}^5$, is best prepared by adding 1 mol. chloral hydrate to 1 mol. potassium cyanide under absolute alcohol, whereupon a brisk action takes place, accompanied by evolution of hydrocyanic acid:



and



Water added to the product separates a heavy oil, from which, by fractional distillation, ethyl dichloracetate is obtained, boiling between 164° and 167° .

From this ether dichloroacetic acid may be conveniently prepared by mixing 1 mol. of the ether, diluted with about an equal volume of alcohol, with a pure alcoholic solution of 1 mol. potassium hydrate, whereby it is converted into a thick crystalline pulp of potassium dichloracetate; subjecting this salt in a combustion-tube to the action of hydrochloric acid gas, which it quickly absorbs; and finally heating the product in a slow stream of the gas. Dichloroacetic acid then distils over, as a liquid which boils at 189° – 191° , and solidifies below 0° . The quantity obtained is very nearly equal to that required by theory (Wallach, *Deut. Chem. Ges. Ber.* vi. 114; ix. 1213; x. 477; compare Cech a. Schwebel, *ibid.* x. 288).

The compound which Amato obtained (2nd Suppl. 9) by treating ethyl dichloracetate, dissolved in alcohol, with a slightly acidulated solution of potassium cyanide, and supposed to have the composition $\text{CH}(\text{CONH}^2)^2.\text{CO}^2\text{C}^2\text{H}^5$, has been found, on further examination, to be merely allophanic ether, $\text{C}^2\text{H}^2\text{N}^2\text{O}^2.\text{C}^2\text{H}^5$, resulting from the action of potassium cyanate contained in the crude cyanide on the alcohol used as a solvent (*Gazz. chim. ital.* iii. 469).

Trichloroacetic Acid, $\text{CCl}^3.\text{COOH}$.—A. Clermont (*Ann. Ch. Phys.* [5], ii. 401; *Compt. rend.* lxxvi. 774; lxxx. 1270), prepares this acid by oxidation of chloral hydrate, either with chromic or with nitric acid, or with potassium permanganate. (a.) A strong solution of chromic acid is poured by small portions into a cooled strong solution of chloral hydrate; one half of the liquid is saturated with potash, then mixed with the other half; and the solution is left to evaporate, whereupon potassium trichloroacetate crystallises out in octahedrons. (b.) Chloral hydrate is mixed with 3–4 times its weight of fuming nitric acid, and the liquid is left to itself for 3 to 15 days, according to the temperature and the brightness of sunshine to which it is exposed. On distillation the boiling point rises to 195° , where it remains constant. A clear distillate is thus obtained which solidifies at 44.8° , with a rise of temperature to 52.4° . (See also Tommasi a. Meldola, *Chem. Soc. Jour.* [2], xii. 314). (c.) The concentrated solution of 1 mol. potassium permanganate and 2 mols. chloral hydrate are mixed together, whereby acid trichloroacetate of potassium is produced; and the solution of this salt, freed by filtration from brown manganese oxide, is distilled with concentrated phosphoric acid; the liquid which passes over at 195° consists of pure trichloroacetic acid (Clermont).

The metallic trichloracetates are usually prepared by neutralising the carbonates or oxides with trichloroacetic acid. Clermont has also prepared the neutral and acid potassium salts by oxidising chloral with potassium permanganate; these salts are nearly all crystallisable, but decompose when their aqueous solutions are heated. They may be crystallised by evaporation over caustic lime, or sulphuric acid, or by exposing saturated solutions to the varying temperature of day and night.

The trichloracetates of iron and cobalt are not crystalline; the neutral potassium, calcium, and thallium trichloracetates, crystallise in needles; the acid potassium, ammonium, and thallium trichloracetates, in octohedrons; the neutral ammonium, lithium, strontium, nickel, and lead salts form prismatic crystals; the barium, zinc, and silver salts crystallise in small tables; sodium trichloroacetate resembles the acetate, and copper trichloroacetate has a form similar to copper sulphate, while the magnesium and aluminium salts form crystalline crusts.

The *mercurous salt*, $(C^2Cl^3O^2)^2Hg^2$, falls as a white precipitate on mixing potassium trichloroacetate with mercurous nitrate; by washing it quickly, dissolving it in a large quantity of water, and leaving the solution to evaporate, it is obtained in tufts of small crystals. The *mercuric salt*, $(C^2Cl^3O^2)^2Hg$, crystallises from a solution of yellow mercuric oxide in trichloroacetic acid in prismatic needles, slightly soluble in water, easily in alcohol and ether. The *zinc salt*, $(C^2Cl^3O^2)^2Zn + 6H^2O$, separates from solution, after prolonged exposure over lime, in shining micaceous, very deliquescent laminae. *Trichloroacetate of urea*, $C^2HCl^3O^2.CON^2H^4$, separates in brittle plates from a mixture of the solutions of trichloroacetic acid and urea in absolute alcohol (Clermont).

Potassium trichloroacetate heated with bromine to 110° – 120° in sealed tubes for six hours is decomposed, with formation of bromotrichloromethane:



A small quantity of carbon trichloride, C^2Cl^3 , appears also to be formed.

Chlorine and *iodine chloride* act but very slowly on potassium trichloroacetate under similar circumstances, yielding, after prolonged heating, only a small quantity of a heavy oil, probably CCl^3I . With *iodine*, a small quantity of a crystalline body is obtained resembling C^2Cl^3I , and probably consisting of the corresponding iodine compound (van't Hoff, *Deut. Chem. Ges. Ber.* x. 678).

Trichloroacetic acid is converted by PCl^3 into trichloroacetyl chloride, $C^2Cl^3O.Cl$ (b. p. 118°), by *bromine* and *phosphorus*, into $C^2Br^3O.Br$. When *phosphorus tri-iodide* is added to fused trichloroacetic acid, hydrogen iodide and much free iodine are evolved, and a brown distillate is obtained, which is nearly decolorised by mercury, and appears to boil at about 180° . It is decomposed slowly by water, quickly by alcohol, with formation of ethylic trichloroacetate (H. Gal, *Compt. rend.* lxxvi. 774).

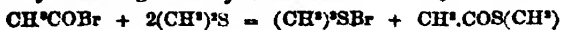
On the decomposition of ethyl trichloroacetate by sodium ethylate, see Klien (*Jenaische Zeitschr. f. Naturw.* x. 63; *Chem. Soc. Jour.* 1877, i. 291).

Chlorobromoacetic Acid, $C^2H^2ClBrO^2 = CHClBr-COOH$.—Produced by heating 1 mol. monochloroacetic acid with 2 at. bromine in sealed tubes to 160° , opening the tubes from time to time to relieve the pressure of the evolved hydrogen bromide, and afterwards heating the mixture till the reaction is complete. The transparent and colourless product, which boils at 200° – 230° , yields, by fractional distillation, pure chlorobromoacetic acid, boiling at 201° . The acid does not crystallise; it has a pungent odour, and destroys the epidermis. All its salts are easily soluble in water; the *silver salt* crystallises in needles, and its solution quickly decomposes, with separation of chloride and bromide of silver.

Ethyl chlorobromoacetate is easily produced by heating an alcoholic solution of the acid in a reflux apparatus standing in the water-bath. It is a colourless liquid, boiling, with partial decomposition, at 160° – 163° , and having an agreeable odour of peppermint. Treated with aqueous ammonia, it yields the amide, $CHClBr-CONH^2$, which crystallises in long needles, melting at 126° (Cech a. Steiner, *Deut. Chem. Ges. Ber.* viii. 1174).

ACETIC BROMIDE or **ACETYL BROMIDE**, C^2H^3BrO . This body unites with *aldehyde*, C^2H^2O , forming the compound $C^4H^5BrO^2$, which is also produced by the action of phosphorus pentabromide on aldehyde. It boils with partial decomposition between 135° and 146° (Tawildarow, *Deut. Chem. Ges. Ber.* vii. 731).

Acetyl bromide, heated to 100° in a sealed tube with *methyl sulphide*, yields a heavy oil, which, on cooling, deposits crystals of trimethylsulphine, the remaining liquid apparently consisting of methyl thiocetate:



(Cahours, *Compt. rend.* lxxxi. 1163).

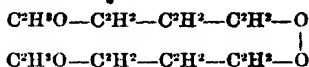
Trichloracetyl bromide, C^3Cl^3OBr , formed by the action of bromine and amorphous phosphorus on trichloroacetic acid, boils, after rectification, at 143° , and is decomposed by water, with formation of trichloroacetic acid, by alcohol with formation of ethyl-trichloroacetate (Gal, *Bull. Soc. Chim.* [2], xx. 41).

ACETIC CHLORIDE or ACETYL CHLORIDE.—*Action of Zinc.*—Gerhards obtained by this reaction a brown amorphous product, together with zinc chloride; Tommasi a. Quesneville (*Compt. rend.* lxxvi. 486) have obtained a body which they term *acetylde*, having the composition C^2H^2O . It may be purified by evaporating off the excess of acetyl chloride, dissolving the residue in alcohol, and precipitating with water, the process being repeated several times. It is soluble in alcohol, ether, hydrochloric acid, fuming nitric acid, acetic anhydride, and chloroform; combines with bromine; does not reduce eupropotassic tartrate.

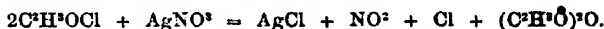
Tommasi a. Quesneville suppose that this body is formed, together with water and acetic acid, by the reaction—



and attribute to it the structure—

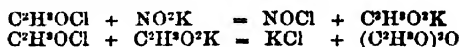


Action on Nitrates and Nitrites.—Silver nitrate is immediately attacked by acetic chloride with evolution of heat, the products being acetic anhydride, together with silver chloride, nitrogen tetroxide, and free chlorine:



Similar results are obtained with other nitrates. Mercuric nitrate, lead nitrate, and potassium nitrate are attacked immediately; barium nitrate is not affected, but calcium nitrate is readily acted upon by acetic chloride. In the case of potassium nitrate, the gas evolved at the beginning of the reaction consists almost wholly of chlorine, the nitrogen tetroxide appearing only towards the end.

Potassium nitrite is readily attacked by acetic chloride, giving off a gas which resembles chlorine in appearance, but appears to consist of nitrosyl chloride. Towards the end of the reaction nitrogen dioxide is also given off. The reaction probably takes place in two stages, according to the equations:



(Armstrong, *Chem. Soc. J.* [2], xi. 683).

ACETIC OXIDE or ANHYDRIDE, $(C^2H^2O)^2O$.—Respecting the action of this compound, and of acetic acid, on ammonium thiocyanate, see **PERTHIOCYANIC ACID and THIOCYANATES**.

ACETIC PHOSPHIDES (A. Steiner, *Deut. Chem. Ges. Ber.* viii. 1178).—The compound $C^2H^2O.PH^2$, analogous to acetamide, does not appear to be formed by the action of acetic chloride on phosphine, the only products of this action being hydrochloric acid and solid phosphide of hydrogen.

Monochloroacetic Phosphide, $C^2H^2ClO.PH^2 = CH^2Cl-COPH^2$, is prepared by passing phosphine gas into monochloroacetic chloride as long as the gas-bubbles can make their way through the resulting mass. This mass is then kneaded in a mortar with cold water, till it falls to a uniform yellowish-white powder, which is then dried in a vacuum, dissolved in ether-alcohol, and the solution is evaporated under the air-pump.

Monochloroacetic phosphide is a white powder with a tinge of yellow; in the moist state it is slowly resolved into phosphine and chloroacetic acid:



Its alcoholic solution, evaporated over the water-bath, leaves a strongly acid syrup, which no longer solidifies. The phosphide heated on platinum foil takes fire and leaves a residue of charcoal.

Trichloroacetic Phosphide, $C^2Cl^3O.PH^2$, also called *Chloroacetylphide*, was obtained by Cloez in 1846, by the action of phosphine on trichloroacetic chloride, and on ethylic perchloroformate, $CCl(C^2Cl^3)O^2$, which splits up when heated into carbonyl chloride and trichloroacetic chloride (i. 979).

ACETIC PICRATE, or ACETYL PICRATE, $C^2H^3O \cdot C^2H^2(NO^2)_2$. When

1 part of picric acid and 4 parts of acetic anhydride are heated in a reflux-apparatus for two hours, a yellowish liquid is obtained, which consists of acetic anhydride holding acetyl picrate in solution. On adding water, this compound is precipitated as a yellowish-white crystalline powder, which is to be washed with water and dried, first by pressure and then in a vacuum. Acetyl picrate melts at 75° – 76° , becoming pale yellow and oily; at 120° it gives off acetic acid; at 180° it darkens, and at 260° it completely decomposes. It is soluble in ether, alcohol, and ethyl acetate, in sulphuric, nitric, and hydrochloric acids. A few hours' exposure to air, and even less when in contact with water, causes it to become yellow, owing to partial decomposition. With an alkali it splits up into picrate and acetate of the alkali-metal. The ethereal solution, when evaporated, deposits beautiful crystals of a deep yellow colour. Acetyl picrate does not detonate when struck, unless mixed with potassium chlorate, in which case it explodes with violence (Tommasi a. David, *Compt. rend.* lxxvii. 207).

ACETIC SULPHITE, or ACETYL SULPHITE, $(C^2H^3O)^2SO^2$, is obtained by dropping acetic chloride on dry lead sulphite, and subsequent distillation. It is a colourless, strong-smelling liquid, which is decomposed by water into sulphurous and acetic acids (Tommasi, *Chem. News.* xxix. 280).

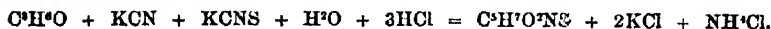
ACETO-ACETIC ETHERS. See p. 11.

ACETOCHLORHYDROSE, $C^2H^2(C^2H^3O)^4ClO^2$.—On the action of nitric acid on this body, see GLUCOSE, under SUGARS.

ACETOGLYCOLCHLORHYDRIN, $C^2H^4 \cdot \begin{matrix} OC^2H^3O \\ Cl \end{matrix}$, is produced by heating 1 part of ethylene hydrochloride (glycol-chlorhydrin), $C^2H^4 \cdot \begin{matrix} OH \\ Cl \end{matrix}$, with $1\frac{1}{2}$ part of acetic anhydride to 110° in a sealed tube (Ladenburg a. Demole, *Deut. Chem. Ges. Ber.* vi. 1023).

ACETONE, $CO(CH^3)^2$.—*Formation from Glycerin.* The product $C^2H^4Cl^2Br^2O$, obtained by the action of bromine on dichlorhydrin, is slowly converted into acetone by the action of zinc and diluted sulphuric acid at about 40° , a brominated compound (probably isopropyl bromide) being formed at the same time (Lange, *Deut. Chem. Ges. Ber.* vi. 98).

Reaction with Cyanides and Thiocyanates.—On adding hydrochloric acid to a mixture of potassium cyanide, potassium thiocyanate, and acetone, the compound $C^2H^3O^2NS$ is obtained—



When heated with hydrochloric acid, it is resolved into acetic acid, carbonic anhydride, and ammonia. With silver nitrate it yields the silver derivative, $C^2H^3AgO^2NS$ (Urech, *Deut. Chem. Ges. Ber.* vi. 1113).

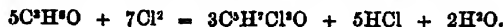
On the Condensation-products of Acetone, see MESITYL OXIDE and PHORON.

BROMACETONES.—Monobromacetone is obtained by adding the required quantity of bromine to a solution of one part of acetone in 10 parts of water. It is a colourless, refractive liquid having a very irritating smell; it is decomposed by heat, but may be distilled with steam; it forms a crystalline compound with acid sodium sulphite, and a crystalline but very unstable compound with dry ammonia, while aqueous ammonia converts it into basic compounds. Dibromacetone has a less pungent smell, and combines with acid sodium sulphite. On adding bromine to a well-cooled aqueous solution of acetone, the compound $C^2H^3OBr^2$ is formed, which has previously been observed by Linnemann; it explodes when freed from water (Sokolowsky, *Deut. Chem. Ges. Ber.* ix. 1687; compare 1st *Suppl.* 2f; 2nd *Suppl.* 13).

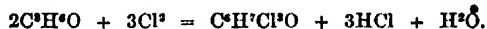
CHLORACETONES (Kraemer, *Deut. Chem. Ges. Ber.* vii. 2f2; Barbaglia, *ibid.* vii. 467; C. Bischoff, *ibid.* viii. 1329). The products obtained by the action of chlorine on acetone differ according to the degree of purity of the acetone employed. With perfectly pure acetone separated from the disulphite-compound, the chlorination does not go beyond trichloracetone, whereas with the so-called pure acetone, found in commerce, which boils at 56° – 58° , and still retains methyl alcohol not separable by fractionation or by calcium chloride, the chlorination goes as high as tetrachloracetone. Commercial acetone is also more readily attacked by chlorine than the pure compound, and assumes a green colour at an early stage of the reaction, whereas pure acetone remains colourless till completely saturated with chlorine (Bischoff).

According to Grabowski (*Deut. Chem. Ges. Ber.* viii. 1436), when pure acetone

(b. p. 56°-57°) is treated with dry chlorine at ordinary temperatures, then heated to 100° in the stream of chlorine, and lastly distilled, large quantities of water and dichloracetone pass over below 170°, and then between 170° and 180° a liquid, which when treated with a very weak solution of potassium dichromate and sulphuric acid, then washed with water, with dilute potash, and again with water, and afterwards dried over calcium chloride and several times fractionally distilled, ultimately yields a nearly colourless liquid of sp. gr. 1.330 at 29°, boiling at 186°, and having the composition of amylic chloral, $C^5H^7Cl^2O$, vapour-density 6.55 (calc. 6.9). The formation of this compound may be represented by the equation:



The portion of the original distillate boiling between 180° and 210° was decolorised by chromic acid mixture, then washed with water, and distilled with over-heated steam at 180°, whereby a nearly colourless liquid was obtained, which passed over between 200° and 230°, and was separable by repeated fractional distillation into six portions, boiling respectively below 200°; between 200° and 205°; 205° and 210°; 210° and 215°; 215° and 220°; and above 220°; the thermometer remaining constant for the longest time between 210° and 215°. This fraction exhibited nearly the composition and vapour-density of trichloromesityl oxide, $C^6H^4Cl^3O$ (vap. dens. obs. 7.55; calc. 7.05). This compound is a nearly colourless heavy liquid, boiling at 206°-208°, and having a sp. gr. of 1.326 at 26°, and a sharp pungent odour like that of dichloracetone. It becomes violet-coloured during distillation, but colourless again on cooling. Strong potash attacks it violently, forming a brown resinous product, having an aldehydic odour. Strong sulphuric acid decomposes it completely, with evolution of hydrochloric acid. Its formation is represented by the equation:



Dichloracetone, $C^3H^4Cl^2O$. This compound is obtained very nearly pure by saturating pure acetone with dry chlorine at low temperatures. The hydrochloric acid, which is absorbed by the product in considerable quantity, is most easily removed by digestion in an apparatus with reflux condenser. The resulting liquid, which is perfectly colourless, begins to boil at 125°, and passes over for the most part at 130°—yields, after a few fractionations, perfectly pure dichloracetone, as a liquid boiling at 120°, and having an agreeable, somewhat pungent odour, with sweet after flavour.

If the acetone be not well cooled during the passage of the gas, or the chlorine not absolutely dry, and if the product be finally warmed and saturated with chlorine in sunshine, trichloracetone is likewise formed in quantity about equal to that of the dichloracetone. Acetone containing methyl alcohol likewise yields dichloracetone when treated as above, but the product consists chiefly of the more highly chlorinated acetones.

Dichloracetone admits of two modifications, viz.:



the latter being formed, as above described, by the action of chlorine on acetone, the former by oxidation of symmetric dichlorhydrin (2nd Suppl. 14). Both of these varieties admit of polymerisation, the unsymmetrical variety apparently in two modifications, the symmetrical in one.

Unsymmetrical Polymerides.—E. Mulder, in preparing ordinary dichloracetone by the electrolysis of a mixture of acetone and hydrochloric acid, obtained also an isomeric body boiling at 135°-140°, which he called *isodichloracetone* (*Deut. Chem. Ges. Ber.* v. 1009). The same modification has been separated by Bischoff, from the portion of the product of the action of chlorine on acetone at low temperatures, which boils at 130°-180°, and is intermediate in composition between di- and tri-chloracetone. On mixing this liquid with water, and exposing it for some time to a low temperature, a solid hydrate of trichloracetone separated out, and the remaining liquid, subjected to repeated fractional distillation, yielded successively portions boiling at 140°-150°, 135°-140°, and 132°-135°. The composition of these products follows:—

	B.-p. 140°-150°	B.-p. 135°-140°	B.-p. 132°-135°	$C^3H^4Cl^2O$
C	26.97	28.1	27.9	28.3
H	2.87	2.9	3.0	3.1
Cl	56.35	55.7	56.1	55.6

The first portion is intermediate in composition between di- and trichloracetone. The second and third have the composition of dichloracetone, and are regarded by Bischoff as a polymeride of the unsymmetrical modification of that compound.

A solid polymeride is described by Barbaglia (*Deut. Chem. Ges. Ber.* vii. 467) as likewise formed by the action of chlorine on acetone at low temperatures. Chlorine gas was passed into acetone kept cool by a mixture of ice and salt, in diffused daylight, till the weight of the liquid had increased by about two-thirds. The crude product was thrown into cold water, and neutralised with marble, and the liquid was then distilled with steam. The distillate formed two layers, the lower of which was dehydrated by calcium chloride, and submitted to fractional distillation. The unaltered acetone was again acted upon by chlorine, and the total product divided by fractional distillation into six parts. In the part obtained between 140° and 170° large fine prisms appeared in the course of a few hours, having a melting point of 44°. These crystals are easily sublimed, and volatilise in the air. They are insoluble in water, but easily soluble in alcohol and ether. The alcoholic solution shows very clearly the phenomenon of supersaturation. The crystals, well dried between filter-paper, are inodorous, and give by analysis numbers agreeing with the formula of dichloracetone.

Three determinations of vapour-density, made with Hofmann's apparatus, at 198°, and with different quantities of substance, gave the numbers 69·67, 79·72, and 113·36 ($H=1$); the formula $C^2H^4Cl^2O$ requiring 63·6, and $C^2H^4Cl^3O$ requiring 127. These numbers show that the substance had not been completely volatilised; but they indicate also that its constitution is polymolecular and probably bimolecular.

Symmetrical Polymerides.—In preparing symmetrical dichloracetone by the oxidation of dichlorhydrin, Bischoff obtained an oily distillate of pungent odour, which, after a considerable time, changed into white crystals, giving by analysis 55·7 per cent. chlorine, the formula of dichloracetone requiring 55·9. As Glutz a. Fischer (*2nd Suppl.* 14) found the boiling point of this liquid modification to be between 170° and 171°, it is doubtless a polymeric symmetrical dichloracetone; and the crystalline modification formed from it is probably also a polymeride (Bischoff).

The number of known modifications of dichloracetone appears, therefore, to be five, namely:—

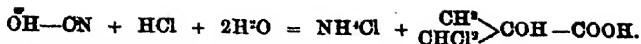
- | | |
|---|----------------|
| 1. Unsymmetrical dichloracetone, $C^2H^4Cl^2O$, boiling at 120°. | |
| 2. Liquid polymeride thereof | " " 135°—140°. |
| 3. Solid | " " 140°—170°. |
| 4. Symmetrical polymeride, liquid | " " 170°—171°. |
| 5. " " solid | " " |

There is, however, some uncertainty about the existence of the solid unsymmetrical polymeride described by Barbaglia, as Bischoff was unable to obtain it.

Dichloracetone-cyanhydrin, $C^2H^4Cl^2NO = \begin{smallmatrix} CH^3 \\ | \\ CHCl \end{smallmatrix} > COH-CN$ (Bischoff, *Deut. Chem. Ges. Ber.* viii. 1333).—Dichloracetone (b. p. 120°), mixed with an excess of strong aqueous hydrocyanic acid, dissolves to a considerable extent, and on digesting the mixture for some time in a reflux-apparatus placed in a water-bath, the whole of the dichloracetone is gradually dissolved, forming a clear, somewhat yellowish liquid, which becomes turbid when the excess of the hydrocyanic acid is evaporated off at the heat of the water-bath, and there finally remains a faintly yellowish liquid, which at a higher temperature splits up into hydrocyanic acid and dichloracetone. This liquid, treated with alkalis, gives up hydrocyanic acid, the dichloracetone at the same time turning brown and decomposing, with formation of an alkaline chloride. At low temperatures the oily liquid deposits soft tabular crystals, which, however, cannot be long preserved.

To analyse this compound, the oil was repeatedly dissolved in anhydrous ether; and, after the ether had evaporated, dried over calcium chloride. When thus purified it gave 46·3 per cent. chlorine, and 8·9 nitrogen, the formula $C^2H^4Cl^2NO$ requiring 46·1 and 9·09. The body is therefore an addition-product of hydrocyanic acid and dichloracetone, analogous to those formed by monochloracetone, chloral, and aldehyde (*1st Suppl.* 76; *2nd Suppl.* xvi. 310).

Dichloracetonic or Dichlorisobutyric Acid, $C^2H^4Cl^2O^2 = \begin{smallmatrix} CH^3 \\ | \\ CHCl \end{smallmatrix} > COH-COOH$ (Bischoff, *ibid.* 1334). This acid, which may be regarded as an addition-product of dichloracetone and formic acid, is produced by digesting dichloracetone cyanhydrin at the heat of the water-bath, with moderately strong hydrochloric acid, the cyanogen-group being then gradually replaced by the carboxyl-group:



Several days' digestion is required to complete the reaction. The excess of hydrochloric acid is evaporated over the water-bath, water repeatedly added, and the liquid again evaporated down till the residue no longer contains any free hydrochloric acid. By dissolving this residue in ether, and leaving the ether to evaporate, a brownish oily liquid is obtained, having a strong and pure acid taste, and solidifying after a while to a crystalline mass; and by redissolving this mass in ether, and decolorising with animal charcoal, the dichloroacetic acid is obtained in cauliflower groups of prisms having a splendid silky lustre, or, by addition of alcohol to the ethereal solution and gradual evaporation, in short thick prisms. It melts at 82° - 83° , decomposes more or less when distilled, but may nevertheless be sublimed, and is deposited on the sides of the vessel in radiate groups of prisms.

Ammonium dichloroacetate is produced by neutralising the acid with ammonia, both being dissolved in alcohol, and solidifies after a while to a satiny crystalline mass of felted prisms, or, in presence of a larger quantity of alcohol, in crystalline crusts formed of distinct prisms. This salt is very soluble in water, and decomposes when the solution is heated.

The *potassium salt*, prepared in like manner, separates in broad needles and crystalline crusts; it is moderately soluble in alcohol, very soluble in water, and decomposes, like the other salts, when heated.

The *silver salt*, $\text{C}_2\text{H}_3\text{AgCl}_2\text{O}_2$, separates on adding silver nitrate and a little ammonia to the concentrated solution of the acid, as a white precipitate consisting of small prisms, sometimes growing to needles of considerable length. It is somewhat sparingly soluble in cold water, and separates on evaporation at ordinary temperatures in transparent laminae. On heating the solution, rapid decomposition takes place, with separation of silver chloride, and the undecomposed salt crystallises in rather large prisms.

The *barium salt* is formed by saturation, and separates on evaporation as a hydrated crystalline mass, made up of prisms.

Lead salts.—On dissolving recently precipitated lead carbonate in the acid, and leaving the solution to evaporate, a hydrated neutral lead-salt separates in small yellowish crystalline spherules, and the mother-liquor yields a much more soluble basic salt in groups of rather large transparent prisms.

Ethyl Dichloroacetate, $\text{C}_2\text{H}_4\text{Cl}_2\text{O}_2$, is produced by saturating the solution of the acid in absolute alcohol with dry hydrochloric acid gas, and separates, on addition of water, as a brown liquid. It is, however, partly decomposed by water, and is therefore better separated by evaporating off the alcohol and hydrochloric acid on the water-bath. On attempting to distil it, the thermometer rose quickly to 220° , but the greater portion distilled over between 208° and 215° (Bischoff).

Trichloroacetone, $\text{C}_2\text{HCl}_3\text{O}$. This compound, which Bouis obtained by the action of chlorine on crude wood-spirit containing acetone (i. 30), is also formed by passing chlorine into pure acetone.* This liquid, previously saturated with chlorine at low temperatures, takes up on exposure to sunshine, or when heated, a large additional quantity, especially if the chlorine be not quite dry, the product ultimately consisting of di- and trichloroacetone, boiling respectively at 150° and 170° , together with small quantities of intermediate products. Pure acetone does not form any more highly chlorinated products.

The fraction boiling at 165 - 175° , solidified when mixed with water and exposed to a low temperature, in splendid tablets and short prisms, which, after washing with water, had the composition of trichloroacetone-hydrate, $\text{C}_2\text{HCl}_3\text{O} \cdot 2\text{H}_2\text{O}$, and melted at 43° ; and on passing dry hydrochloric acid gas into the fused hydrate, anhydrous trichloroacetone was obtained boiling at 170° - 172° . Pure trichloroacetone absorbs water rapidly from the air, and is converted into the hydrate. It does not possess the intensely pungent odour attributed to trichloroacetone by Bouis (i. 30), which in fact belongs to another chlorinated derivative of acetone (Bischoff, *Deutsch. Chem. Ges. Ber.* viii. 1329).

Trichloroacetone is also formed by the action of chlorine on the mixed product obtained by oxidising commercial isobutyl alcohol with chromic acid mixture. This product contains acetone formed from the isobutyl alcohol:



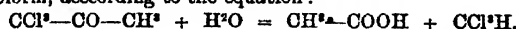
and on passing chlorine into the portion of the liquid which boils between 60° and 70° ,

* It is not produced by the action of chlorine on pure methyl alcohol: hence the trichloroacetone obtained by Bouis must have been formed from acetone contained in the crude wood-spirit of which he operated.

neutralising the crude product with calcium carbonate and distilling, a distillate is obtained consisting of a watery and an oily layer. The watery layer, evaporated at a gentle heat, yields crystals of trichloroacetone hydrate, from which the anhydrous compound may be obtained as above described; and the oil separates on distillation into monochloroacetone, trichloroacetone, and its hydrate (Krämer, *Deut. Chem. Ges. Ber.* vii. 252).

Two modifications of trichloroacetone are possible, represented by the formulæ, $\text{CCl}^3\text{—CO—CH}^3$ and $\text{OH}^3\text{Cl—CO—CHCl}^2$, and both of these might be produced by further chlorination of ordinary dichloroacetone, $\text{CHCl}^2\text{—CO—CH}^3$ (b. p. 120°). They may, however, be distinguished from one another by means of the reaction with alkalis and aniline discovered by Hofmann (2nd *Suppl.* 325), whereby, in the case of compounds containing the group CCl^3 , phenyl-isocyanide or phenyl-carbimide is produced, recognisable by its intense and unmistakable odour; and in fact, on heating a very small quantity of the trichloroacetone hydrate obtained as above with aniline and caustic potash, the peculiar odour is strongly developed.

Trichloroacetone may then be regarded as methylated chloral, and according to this constitution it might be expected to be resolved by water or dilute alkalis into acetic acid and chloroform, according to the equation:

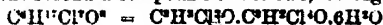


The reaction, however, takes place in quite a different way, the products actually obtained by heating trichloroacetone-hydrate with water in sealed tubes being a brown syrupy substance having a sweetish taste, together with hydrochloric acid, carbon dioxide, and a small quantity of acetic acid, but no chloroform. It seems probable, therefore, that the molecule is completely split up, and a condensation-product formed.

Trichloroacetone has lost by chlorination so much of the aldehydic and ketonic characters of acetone, that it no longer combines with alkaline bisulphites. It unites however with *hydrocyanic acid*, forming trichloroacetone-cyanhydrin, which may be obtained in the same manner as the corresponding dichlorinated compound, in the form of a yellow oily liquid, smelling faintly of its two components. By treatment with hydrochloric acid, this compound is converted into trichloroacetic acid, a syrupy, uncrystallisable, very unstable acid, from which no definite salt can be obtained. The silver salt is formed as a white, moderately soluble precipitate, on adding silver nitrate till no further chlorine reaction is perceptible, and then adding ammonia. The acid is very easily decomposed by alkalis (Bischoff).

Tetrachloroacetone, $\text{C}^2\text{H}^2\text{Cl}^4\text{O}$ (Bischoff, *loc. cit.*)—This compound is not formed from pure acetone, but it is produced, together with the lower chloroacetones, by the action of chlorine on acetone containing methyl alcohol. When chlorine is passed into this impure acetone, the liquid becomes red, brown, yellow, and yellowish-green, and there frequently separates from it, even long before saturation, an oil which deposits hard crystals insoluble in water. These crystals consist of the so-called *chloromercaptate of methylene*, which Bouis obtained by the action of chlorine on wood-spirit, and were regarded by him as a compound of methylic oxide and dichloroacetone. The real nature of this body has not yet been determined. Bischoff however finds, contrary to the statement of Bouis, that it has no influence on the further products of the reaction, which in fact goes on in just the same way after it has been removed.

As the saturation with chlorine proceeds, the product becomes more oily, water collects on the surface, and hydrochloric acid escapes in large quantity. The final product, washed with water—(whereby, however, large quantities are dissolved and lost)—and dried, gave by analysis numbers quite irreconcilable with the formula of trichloroacetone—of which Bouis supposed it to consist—and in fact not leading to any definite formula. To avoid the great loss occasioned by washing with water, Bischoff heated the product in a reflux-apparatus to expel hydrochloric acid, then dried the liquid, which by this time had become black, and submitted it to fractional distillation. Small quantities of dichloroacetone then passed over at 62° , the greater portion of the product at $130^\circ\text{--}220^\circ$, the residue suddenly splitting up at this last temperature, giving off intensely irritating vapours and large quantities of hydrochloric acid, and leaving a spongy carbonaceous mass. The distillate was then further separated into three portions, passing over at $130^\circ\text{--}160^\circ$, $160^\circ\text{--}180^\circ$, and $180^\circ\text{--}210^\circ$, the middle portion being by far the largest; and those fractions were further separated into smaller fractions, which were exposed to a low temperature in contact with water, the crystalline films being removed as they formed, and the remaining oil again exposed to cold in contact with water. By this treatment, the fraction $160^\circ\text{--}180^\circ$ yielded three products, the first of which was pure trichloroacetone hydrate, $\text{C}^2\text{H}^2\text{Cl}^3\text{O} \cdot 0.2\text{H}^2\text{O}$; the third nearly pure tetrachloroacetone-hydrate, $\text{C}^2\text{H}^2\text{Cl}^4\text{O} \cdot 0.4\text{H}^2\text{O}$, and the second a compound of the two, having the composition



On passing dry hydrochloric acid gas into this last hydrate in the fused state, the water is removed, and a liquid remains having the composition $C^3H^4Cl^2O^2$, and separable by distillation into tri- and tetrachloracetone.

That the crystalline body $C^3H^4Cl^2O^2$ is really a definite compound, and not a mere mixture of the hydrates of tri- and tetrachloracetone, is shown by its stability when recrystallised by refrigeration, by its melting point, which is below those of the hydrates of tri- and tetrachloracetone, and by the constancy of its composition.

Tetrachloracetone Hydrate, $C^3H^4Cl^4O.4H^2O$.—The liquid remaining after the compound hydrate just described has crystallised out, solidifies in large prisms, agreeing in external characters and in composition with the tetrachloracetone-hydrate described by Bouis. It melts at 38° – 39° .

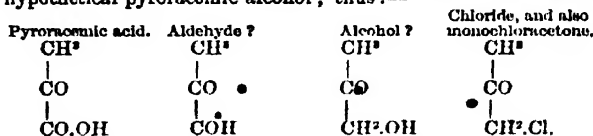
Anhydrous tetrachloracetone is obtained by passing dry hydrochloric acid gas into the fused hydrate. It is an extremely volatile body, having an intensely pungent odour, and volatilising with vapour of water, to which it also imparts its odour. Heated with aniline and potash, it yields phenyl isocyanide; hence its constitution is $CCl^2-CO-CH^2Cl$. It absorbs water with extreme rapidity, but the resulting hydrate remains for some time in a state of surfusion, from which it passes into the crystallised state when touched with a glass rod.

There appears also to be another hydrate of tetrachloracetone, containing less than 4 mols. of water; for when the crystals of the tetrahydrate are left over oil of vitriol they become opaque and covered with a thin felted crystalline web, which disappears quickly on exposure to moist air (Bischoff).

Action of Water and Silver Oxide on the Chlorinated and Brominated Derivatives of Acetone.—Linnemann observed some time ago that formic, acetic, and propionic acids are produced when moist silver oxide is added to a mixture of acetone and bromine (1st Suppl. 27). He has since observed the following facts. When silver oxide is made to react upon an aqueous solution of monochloracetone, a silver salt is formed, which has the formula $C^2H^3Ag^2O^2$, and can be converted into a calcium salt containing $C^2H^3CaO^2 + H^2O$. When pure monochloracetone is heated for ten hours with 6–8 volumes of water at a temperature of 220° – 230° , the whole of the chlorine is expelled as hydrochloric acid, and a non-volatile acid is formed, which, after the removal of the hydrochloric acid and silver, and concentration over sulphuric acid, is obtained as a glassy mass of a faint yellow colour. This substance differs from those which are obtained by the action of silver oxide. When dichloracetone and water react on each other, ordinary lactic acid is formed by exchange of chlorine for hydroxyl.

A repetition of the experiments on the action of moist silver oxide on bromine and acetone, with perfectly pure acetone, showed that the only volatile fatty acids produced are acetic acid and a small quantity of formic acid. Compare Emmerling (2nd Suppl. 13).

Monochloracetone and monobromacetone are sometimes regarded as haloïd derivatives of the hypothetical pyroracemic alcohol; thus:—



According to this view, the replacement of the bromine of monobromacetone by hydroxyl should actually yield pyroracemic alcohol. But it is found that monobromacetone reduces silver oxide, and therefore the action is more probably $C^2H^3BrO + O - HBr = C^2H^3O^2$, yielding pyroracemic aldehyde, which by the further action of the silver oxide is oxidised to pyroracemic acid. The non-volatile acid, $C^2H^3O^2$, observed by Emmerling, may be regarded as a polymeride of pyroracemic aldehyde.

When oxide of mercury was substituted for oxide of silver, and the products of the reaction were treated with a quantity of sodium-amalgam, sufficient to convert any pyroracemic acid that might be present into lactic acid, and the pyroracemic aldehyde and alcohol into isopropyl glycol, the only body obtained was acetic acid (Linnemann, *Wien. Akad. Ber.* lxxiii. 437; *Chem. Soc. Jour.* [2], xii. 1166).

ACETONE, AMMONIA-DERIVATIVES OF. The bases produced by the action of ammonia on acetone have lately been examined by W. Heintz (*Berlin Monatsber.* 1874, 235; *Chem. Centr.* 1874, 372; further, *Annalen der Chemie*, clxxiv. 138; clxxviii. 305, 326; clxxxi. 70; clxxxiii. 276), and by Sokoloff & Latschinoff (*Deut. Chem. Ges. Ber.* vii. 1384). Städeler, in 1858, by saturating acetone with ammonia gas, and heating the solution to 100° in sealed tubes, obtained a basic sub-

stance which he designated as *acetone*, assigning to it the formula $\text{C}^3\text{H}^3\text{N}^3$, and supposing it to be formed by the union of 3 mols. $\text{C}^3\text{H}^3\text{O}$ and 2 mols. NH^3 , with elimination of $3\text{H}^2\text{O}$. The experiments of Heintz have shown, however, that this result is altogether incorrect, and that the action of ammonia on acetone gives rise to three distinct bases, neither of which has the composition of Städeler's acetone, each of them in fact containing in its molecule only one atom of nitrogen. The composition and mode of derivation of these bases is given in the following table:—

Diacetonamine . . .	$\text{C}^3\text{H}^3\text{NO} = 2\text{C}^3\text{H}^3\text{O} + \text{NH}^3 - \text{H}^2\text{O}$
Triacetoneamine . . .	$\text{C}^6\text{H}^6\text{NO} = 3\text{C}^3\text{H}^3\text{O} + \text{NH}^3 - 2\text{H}^2\text{O}$
Dehydrotriacetoneamine . .	$\text{C}^3\text{H}^3\text{N} = \text{C}^3\text{H}^3\text{NO} - \text{H}^2\text{O}$

In Heintz's first paper this last base was named *acetone*. Städeler's acetone is supposed by Heintz to have been impure triacetoneamine.

Sokoloff a. Latschinoff agree with Heintz as to the composition of these three bases; they, however, designate the two oxygenated bases as *diacetonehydramine* and *triacetonehydramine*, and the non-oxygenated base as *triacetoneamine*. We shall adhere to Heintz's nomenclature.

To separate these bases, the liquid obtained by heating acetone with ammonia is neutralised with hydrochloric acid and distilled; the residue is exhausted with absolute alcohol; the solution partially precipitated with platinic chloride; and the precipitate, which contains a portion of the platinum salt of dehydrotriacetoneamine, together with a large quantity of ammonium platinochloride, is separated from the liquid by filtration. On adding to the filtrate an excess of platinic chloride, and then a very large quantity of ether, a new and very copious precipitate is formed, consisting of the platinochlorides of the two oxygenated bases, and a small quantity of the platinochloride of dehydrotriacetoneamine. On dissolving this precipitate after washing with ether-alcohol, in the smallest possible quantity of lukewarm water, a portion of the last-named platinum salt remains behind, and the filtered liquid, on cooling, deposits splendid golden-yellow needles of the platinochloride of triacetoneamine, a further quantity of which may be obtained by evaporation under reduced pressure. At the same time, however, short thick prismatic crystals of another salt are formed, which must be separated mechanically. A portion of the platinochloride of triacetoneamine appears also to be reduced to platinochloride (Heintz).

Sokoloff a. Latschinoff leave a saturated solution of ammonia in acetone to stand at ordinary temperatures for three or four weeks; then add to it a quantity of finely pounded oxalic acid, sufficient to form an acid salt, and a quantity of water equal to that of the acetone employed. A crystalline precipitate is then immediately formed, which is easily separated by means of boiling alcohol (of 95°), into insoluble ammonium oxalate and soluble oxalate of diacetoneamine, $\text{C}^3\text{H}^3\text{NO}$; 100 grams of acetone yield in this manner from 40 to 50 grams of this salt, and about 10 per cent. more may be obtained by evaporating the mother-liquor, and treating the residue with the alcohol which has served for the separation of the first precipitate. By further boiling with the same alcohol, a mixture of salts is obtained, from which, after conversion into platinum salts, the platinochloride of triacetoneamine may be separated; and the alcoholic mother-liquor, which no longer gives crystals of the above-mentioned salts, forms, after evaporation of the alcohol, a dark-brown tarry mass, which, when distilled with aqueous potash, yields dehydrotriacetoneamine, $\text{C}^3\text{H}^3\text{N}$.

Diacetonamine, $\text{C}^3\text{H}^3\text{NO}$, is best prepared, according to Heintz, by passing dry ammonia gas into a flask containing acetone in a state of gentle ebullition, the conducting tube not dipping into the liquid, but terminating just above it—conducting the mixture of acetone vapour and ammonia through a tube heated to 100° , and then through a condensing tube. The distillate thus obtained is neutralised with sulphuric acid diluted with an equal volume of water; and after removing the ammonium sulphate which crystallises out, and distilling off unaltered acetone, the liquid is evaporated to dryness and the residue exhausted with boiling alcohol: diacetoneamine sulphate then crystallises out on cooling, and may be purified by recrystallisation from alcohol. The mother-liquors contain the sulphate of another base not yet examined.

Diacetonamine dissolves more readily in cold than in warm water, and is partly decomposed by distillation, with formation of ammonia and, apparently, mesityl-oxide. It becomes brown on exposure to the air, and appears to absorb oxygen (Heintz).

The *hydrochloride*, $\text{C}^3\text{H}^3\text{NO} \cdot \text{HCl}$, dissolves very easily in alcohol, still more easily in water, even at ordinary temperatures, and separates, by slow evaporation over sulphuric acid, in rather large well-defined rhombic prisms, which are anhydrous and do not decompose at 100° . The *platinochloride*, $2(\text{C}^3\text{H}^3\text{NO} \cdot \text{HCl}) \cdot \text{PtCl}_4$, crystallises

from aqueous solution in splendid orange-coloured monoclinic prisms (S. and L.), rhombic (Heintz), containing 2 mols. water of crystallisation. It is moderately soluble in hot alcohol, and separates from the solution in brown prismatic anhydrous crystals (Sokoloff & Latschinoff), in orange-yellow monoclinic crystals containing 2 mols. water (Heintz).

The alcoholic solution exposed to sunlight loses its colour, and deposits a small quantity of platinum. The solution in alcohol containing hydrochloric acid becomes much darker, under the same conditions, and if examined after several days' exposure, is found to contain nothing but *diacetoneamine platinosochloride*, $C^6H^{11}N^2O^2Cl^2Pt$, which crystallises in red-brown needles, easily soluble in water and hot alcohol, insoluble in ether (Heintz).

The *neutral sulphate* is very easily soluble both in alcohol and in water. The alcoholic solution deposits anhydrous crystals, which are unaltered at 100° . The *picrate* dissolves with some difficulty in cold water. Hot solutions yield golden-yellow needles several centimeters long, and containing one molecule of water, which they lose at 100° (S. and L.)

The *acid oxalate*, $C^6H^{11}NO.C^2H^2O^4 + H^2O$, forms large monoclinic prisms easily soluble in hot, less soluble in cold water. The *neutral oxalate*, $(C^6H^{11}NO)^2.C^2H^2O^4$, is rather less soluble than the acid salt.

The salts of diacetoneamine, treated with potassium nitrite, yield mesityl-oxide, and the same body is produced, together with ammonia, when they are decomposed by alkalis (S. and L.)

Triacetoneamine, $C^6H^{11}NO$. This base is formed, together with diacetoneamine, by the action of ammonia on acetone, the proportions in which the two are produced depending on the temperature. At low temperatures the product consists almost entirely of diacetoneamine, but at higher temperatures triacetoneamine is largely formed. Moreover, diacetoneamine, when heated with acetone, is converted into triacetoneamine, the yield of the latter being especially large when diacetoneamine is boiled for some time with acetone in a reflux apparatus, the conversion of the diacetoneamine being then almost complete. This is regarded by Heintz as the best mode of preparing triacetoneamine.

For separating the two bases when mixed, the methods above given, founded on the difference of solubility of the platinosochlorides in alcohol, are both troublesome and expensive. The separation may be much more easily effected by taking advantage of the great difference of solubility in water of the neutral oxalates, the diacetoneamine oxalate being by far the more soluble of the two.

The mode of proceeding differs according as the tri- or diacetoneamine predominates. *a.* A mixture of the former kind is the syrupy liquid which remains in the flask in which acetone is boiled in contact with ammonia gas for the preparation of diacetoneamine, as already described (p. 28). This liquid is to be mixed with alcohol, and hydrated oxalic acid gradually added to slight acid reaction. The precipitate, consisting of the oxalates of the two bases, sometimes mixed with ammonium oxalate, is pressed and dissolved in water; the resulting solution is evaporated over the water-bath, with frequent stirring, till a considerable quantity of salt has separated out; and this salt is quickly drained and washed in a vacuum-filter with a small quantity of hot water. The filtered liquid deposits nothing on cooling, unless ammonium oxalate is present, in which case the deposited salt must be drained, and the liquid further evaporated, until, finally, a mother-liquor is obtained, which no longer deposits any oxalate of triacetoneamine or oxalate of ammonia. By repeating these operations on the entire crop of triacetoneamine oxalate, this salt is obtained quite free from the oxalates of ammonia and diacetoneamine, and if the solution has also been treated with animal charcoal, it is perfectly colourless.

b. The mother-liquor contains the whole of the diacetoneamine, together with considerable quantities of triacetoneamine, and traces of ammonia. For the further separation of these bases, oxalic acid is added in quantity about half sufficient to saturate them; the whole is evaporated to dryness; the excess of oxalic acid is removed by washing with cold absolute alcohol; and the residue is boiled with absolute alcohol, whereby a portion of the acid oxalate of triacetoneamine—larger or smaller according to the quantity of alcohol used—is converted into the neutral salt, which is insoluble in boiling alcohol. The solution is filtered at the boiling heat, and the residue washed with boiling alcohol. Neutral oxalate of triacetoneamine then remains on the filter, and the filtered alcoholic solution deposits crystals of acid oxalate of diacetoneamine mixed with a small quantity of the triacetoneamine salt.

These methods of separation are, however, not convenient for the preparation of triacetoneamine, which, indeed, is best obtained, as already stated, by boiling diacetoneamine with acetone.

Triacetoneamine separates from a solution of the neutral oxalate mixed with

caustic potash, as a hydrate, $C^6H^{11}NO \cdot H^2O$, which crystallises from hydrous ether in large square tablets; and the mother-liquor of this hydrate yields, on further evaporation and cooling to a very low temperature, long needle-shaped crystals of anhydrous triacetoneamine. The mother-liquor of this mixed with a few drops of water, again deposits crystals of the hydrate; and finally there remains a mother-liquor containing an uncrystallisable modification of triacetoneamine.

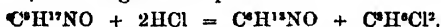
The tabular crystals belong to the orthorhombic system.

Brachydiagonal	Macrodiagonal	Principal axis
0.9586	0.9798	$\frac{1}{2}$

Combination $OP \cdot 2P^\infty \cdot 2P^\infty$. Angle $OP : 2P^\infty = 116^\circ 24'$; $OP : 2P^\infty = 116^\circ 36'$. Cleavage parallel to OP . The crystals, in consequence of the near approach to equality of the lateral axes, have very nearly the appearance of the quadratic combination $OP.P$, but their behaviour to polarised light shows that they are really orthorhombic.

The tabular crystals of the hydrate melt at 58° , the anhydrous needles at 34.6° . Triacetoneamine volatilises slowly even at ordinary temperatures, and in a warm room it sublims from place to place in the containing vessel. It may be distilled without decomposition.

Triacetoneamine is decomposed by heating to 150° – 200° with strong sulphuric acid, or with phosphoric anhydride, but does not yield definite products. Heated to 100° for eight to sixteen hours, with 8–10 parts of fuming hydrochloric acid, it yields a considerable quantity of diacetoneamine together with tetrahydropentacetoneamine (p. 31) and other products. The formation of diacetoneamine is most probably attended with that of methylchloroacetol, $C^3H^6Cl^2$, or its decomposition-product chloropropene, C^3H^4Cl , according to the equation:



These bodies have not however been detected in the product of the reaction, and may therefore be supposed to have acted on a portion of the diacetoneamine, giving rise to hydrogen chloride and more highly carbonised bases, which are in fact present in the crude product.

Salts of Triacetoneamine.—The *hydrochloride*, $C^6H^{11}NO \cdot HCl$, obtained by direct combination, or by decomposing the platinochloride with hydrogen sulphide, remains, on evaporating its solution over the water-bath, as a colourless syrup, which solidifies on cooling to a radiate mass of small transparent prismatic crystals. It is easily soluble in alcohol, especially when hot, and separates from the alcoholic solution at 35° , on addition of ether, in crystals rather larger than those which are deposited from the aqueous solution.

The *platinochloride*, $2(C^6H^{11}NO \cdot HCl) \cdot PtCl^4 + 3H^2O$, crystallises in long dark golden-coloured needles, easily soluble in boiling water, nearly insoluble in alcohol and insoluble in ether. It is easily soluble in alcohol to which hydrochloric acid has been added, and crystallises from this solution with only 1.75 per cent. of water, or less than one molecule. By exposing the solution in alcohol and hydrochloric acid to sunlight, or by heating the aqueous solution for several hours, the salt is reduced to the *platinoso-chloride*, $2(C^6H^{11}NO \cdot HCl) \cdot PtCl^2 + 2H^2O$, which crystallises in dark red needles, and sometimes in rhombic prisms. It is much less soluble in water than the platinochloride.

The *sulphate*, $(C^6H^{11}NO)^2SO_4H^2$, obtained by neutralising dilute sulphuric acid with the base, and evaporating, crystallises in delicate needles or prisms, very freely soluble in water either hot or cold, insoluble in alcohol and in ether.

The *nitrate*, $C^6H^{11}NO \cdot NO_3H$, crystallises by spontaneous evaporation of a solution concentrated by heat, in rhombic crystals exhibiting the combination $P.OP.2P^\infty.P^\infty$. Ratio of lateral and vertical axes = 1.27382 : 1 : 1.0251. Angle $OP : P = 59^\circ 30'$ and $127^\circ 30'$; $P : P$ in the lateral edges = $12^\circ 20'$ and $58^\circ 40'$. The crystals dissolve easily in water, though much less freely than the sulphate, also in alcohol.

The *acetate* is so freely soluble in water that it is not easily obtained in crystals. It dissolves easily in alcohol, and to some extent in ether.

The *neutral oxalate*, $(C^6H^{11}NO)^2C^2O_4H^2$, obtained by evaporating an aqueous solution of the base (11 parts), and oxalic acid (4 parts), crystallises in long glittering needles, easily soluble in cold, and not much more in hot water, very sparingly soluble in alcohol. The crystals are permanent in the air, and may be heated to 100° without decomposition.

The *acid oxalate*, $C^6H^{11}NO \cdot C^2O_4H^2$, obtained by dissolving the neutral salt in water, together with an equivalent quantity of oxalic acid, forms triclinic crystals cleavable in two directions inclined to one another at an angle of $52^\circ 41'$. It is easily

soluble in water, especially when hot. By boiling with alcohol or ether it is resolved into the neutral salt and free oxalic acid.

The *neutral tartrate*, $(C^3H^{11}NO.C^2H^2O_4)$, crystallises from a neutral solution of the base in tartaric acid, in long needles easily soluble in water and in boiling alcohol.

The *acid tartrate* appears to be uncrystallisable. A solution of the neutral tartrate to which an equivalent quantity of tartaric acid has been added, leaves on evaporation a thick syrup, the alcoholic solution of which, when mixed with ether, deposits the neutral salt. The acid tartrate therefore, like the acid oxalate, is resolved by alcohol and ether into the neutral salt and free acid.

Isotriacetoneamine, $C^3H^{11}NO$. This is the uncrystallisable modification contained in the last mother-liquors, which remain after the separation of crystalline triacetoneamine from the oxalate by means of potash (p. 30). The mother-liquors of triacetoneamine platino-chloride sometimes also deposit hemispherical aggregations of small prismatic crystals, which when crystallised always assume the same form. These crystals have the composition $(C^3H^{11}NO.HCl)_2.PtCl^4 + 2H^2O$, the same therefore as that of triacetoneamine platinochloride, except that they contain 2 mols. water instead of three.

On separating the platinum with hydrogen sulphide, and decomposing the resulting hydrochloride with potash or soda and ether, as above indicated, crystals of hydrated triacetoneamine are first deposited, and ultimately a mother-liquor is obtained containing the uncrystallisable base. Heintz regards these crystals as a compound of 1 mol. triacetoneamine hydrochloride, 1 mol. isotriacetoneamine hydrochloride, 1 mol. platonic chloride, and 2 mols. water,

$$\begin{array}{c} C^3H^{11}NO.HCl \\ C^3H^{11}NO.HCl \end{array} \left| \begin{array}{c} PtCl^4 + 2H^2O. \end{array} \right.$$

A complete separation of these isomeric bases, either in the free state or in the form of platinum salts, has not yet been effected; but they may be partially separated by converting the uncrystallisable mother-liquors of the free bases into platinum-salt and digesting this salt with alcohol, which dissolves the platinochloride of isotriacetoneamine, and leaves the double platinochloride undissolved; and by repeating this course of operations several times, a platinochloride is ultimately obtained, which dissolves in alcohol and remains as a syrupy mass on evaporating the solution. This platinochloride decomposed as above yields a base which refuses to crystallise.

- **Dehydrotriacetoneamine**, C^3H^9 , is derived from triacetoneamine by abstraction of H^2O , or from acetone and ammonia in the manner shown by the equation, $3C^3H^7O + NH^3 = 3H^2O + C^3H^9N$. Its platinochloride, $2(C^3H^9N.HCl).PtCl^4$, is present in small quantity in the precipitate of ammonium platinochloride obtained in the preparation of triacetoneamine (p. 28), and may be dissolved out of this precipitate by boiling with water. By cooling and further evaporation of the filtered solution, there are obtained, together with octohedrons of ammonium platinochloride, somewhat larger crystals of the platinochloride of dehydrotriacetoneamine, which may be purified by picking them out and recrystallising. They are oblique rhombic prisms, scarcely soluble in cold, more soluble in warm water (Heintz); small crystals generally united in crusts or nodules, quite insoluble in cold, and only slightly soluble in warm water (Sokoloff & Latschinoff).

Dehydrotriacetoneamine is also found, as oxalate, together with triacetoneamine, in the mother-liquor of diacetoneamine oxalate (p. 28), and may be separated therefrom by distillation with potash. It is an oily liquid, and forms salts which oxidise rapidly in the air.

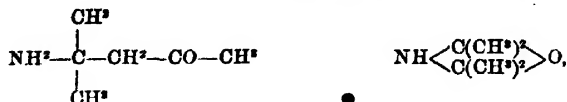
Dehydrotriacetoneamine is not formed by the direct action of dehydrating agents, as sulphuric acid, phosphoric anhydride, &c., on triacetoneamine; its production would appear, therefore, to be due to peculiar conditions present in the preparation of di- and triacetoneamine (Heintz).

The mother-liquor of diacetoneamine oxalate contains also another base, which appears to be dehydrodiacetoneamine, $C^4H^{12}N = 2C^3H^7O + NH^3 - 2H^2O$.

Dehydropentacetoneamine, $C^5H^{22}N = 5C^3H^7O + NH^3 - 5H^2O$, is formed, together with diacetoneamine and other products, by heating triacetoneamine to 100° for eight to sixteen hours, with 8-10 parts of fuming hydrochloric acid. The crude product on cooling deposits an oily liquid, soluble in ether, and containing a base apparently identical with that which separates as a crystalline hydrochloride from the aqueous liquid to which the ether has been added. The salt thus obtained is the hydrochloride of dehydropentacetoneamine, and when treated with fixed alkalis or with ammonia, yields the free base in the form of an oil. This base differs from sparteine, $C^{10}H^{20}N^2$, by the elements of 1 mol. of ammonia (Heintz).

Constitution of the Ammonia-derivatives of Acetone.

Diacetonamine, $C^6H^{11}NO$, may be represented by either of the two following formulæ:—



the first of which is that of an amidogen-base, the second that of an imidogen-base. According to the former, which Heintz regards as the more probable of the two, diacetoneamine has the constitution of acetyl-trimethyl carbamine, or pseudopyramine, $\text{NH}^2-\text{CH}-(\text{CH}^3)^2$, having the hydrogen-atom of the group CH replaced by the ketonic residue, $\text{CH}_2-\text{CO}-\text{CH}^3$.

For the constitution of triacetoneamine, Heintz suggests the two following formulæ:—

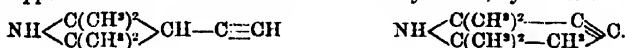


Of these formulæ, both of which represent imidogen-bases, one most probably belongs to triacetoneamine, the other to isotriacetoneamine; but there is no evidence to show which of the two belongs to the crystalline and which to the liquid modification.

Dehydrotriacetoneamine which is derived from triacetoneamine by abstraction of H^2O may, in like manner, be represented by either of the formulæ:—



or, if we suppose two of the carbon-atoms to be trebly linked, by the following:—



Bases formed by Hydrogenation of Di- and Triacetoneamine.—By acting with sodium-amalgam on a solution of diacetoneamine hydrochloride in a mixture of aqueous ammonia and alcohol, diacetonealkamine, $C^6H^{11}ON$, is produced. The free base is a liquid which is soluble in water, has a slight ammoniacal smell, and an aromatic alkaline taste; it boils at $174^\circ-175^\circ$. Its hydrochloride forms a syrupy liquid, and the platinohydrochloride, which is readily soluble in hot water, forms orange-coloured triclinic crystals, $(C^6H^{11}ON.HCl)^2.PtCl^4$. The normal oxalate forms microscopic prisms, and the acid salt crystallises in small plates. When carbon dioxide is passed into a solution of the base in ether, a white precipitate is obtained, crystallising from water in small plates or needles, which seem to be an acid carbonate.

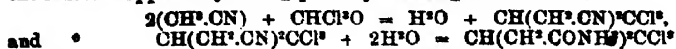
When a solution of triacetoneamine in dilute alcohol is treated with sodium amalgam, it is converted into triacetonealkamine, $C^9H^{15}ON$, and the isomeric pseudotriacetonealkamine. The latter is but sparingly soluble in water and ether, and crystallises from a hot alcoholic solution on cooling. It melts at about 180° , and slowly sublimes. The platinum salt forms rhombic crystals, $(C^9H^{15}ON.HCl)^2.PtCl^4 + 6H^2O$.

Triacetonealkamine crystallises from hot water in apparently quadratic octohedrons and has a slightly sweet and burning taste. It melts at 128.5° , but begins to sublime at 100° . The hydrochloride crystallises from hot water in needles or plates. The platinohydrochloride is freely soluble in water, sparingly in alcohol, insoluble in ether, and anhydrous (Heintz, *Liebig's Annalen*, cxxxiii, 290).

A solution of the platinohydrochlorides of the two preceding bases, in equivalent quantities, yields crystals of a platinum salt having the composition $\left. \begin{array}{l} C^6H^{11}ON.HCl \\ C^9H^{15}ON.HCl \end{array} \right\}.PtCl^4$ (Heintz, *ibid.* 317).

ACETONITRIL. See the last article (p. 28).

ACETONITRIL. *Methyl Cyanide*, $C^2H^3N = CH^3.ON$.—This compound is formed, together with a number of other nitrils and divinyl, $(C^2H^3)^2$, by heating a mixture of acetate and sulphocyanate of lead (Pfankuch, *J. für Chem.* [2], vi, 113). It is not acted upon by chlorine alone, and but slowly in presence of iodine, the product being trichloroacetoneitril (Bacskuns, *Deut. Chem. Ges. Ber.* ix, 1594). Treated with chloral, it yields a crystalline amide having the composition $\text{CH}(\text{CH}^3.CONH^2)^2\text{CCl}^3$, the reaction apparently taking place by two stages:—



(Hübner, *ibid.* vi, 109).

Chlorinated acetonitrils are prepared by distilling the corresponding chlorinated acetamides (2nd Suppl. 4) with phosphoric anhydride, the products being freed from acid by means of potassium carbonate, and finally distilled. They form colourless pungent liquids, insoluble in water, but soluble in alcohol or ether. Treatment with warm dilute mineral acids causes the liberation of ammonia and the formation of the corresponding acids. The chlorinated acetonitrils unite with hydrobromic acid to form crystalline compounds, which are insoluble in ether, but decomposed by water.

Monochloroacetonitril, CH_3ClCN ; boils at $123^\circ\text{--}124^\circ$, has a specific gravity of 1.204 at 11.2° , and a vapour-density of 2.62.

Dichloroacetonitril, CHCl_2CN ; boils at $112^\circ\text{--}113^\circ$, and has a density of 1.374 in the liquid state, and of 3.82 in the state of vapour.

Trichloroacetonitril, CCl_3CN ; boils at $83^\circ\text{--}84^\circ$ (81° Dumas and Leblanc). Its sp. gr. is 1.439, and its vapour-density 5.03. It is remarkable that the trichloro-derivative boils at a lower temperature than the monochloro- or dichloro-derivative, and that the dichloro-derivative boils at a lower temperature than the monochloro-derivative.

When trichloroacetonitril is heated to 100° with alcoholic ammonia, no ammonium chloride or cyanogen is formed, but merely trichloroacetamide (Bischopinck, *Deut. Chem. Ges. Ber.* vi. 731).

Monochloroacetonitril boiled with milk of lime is converted into glycollic acid; dichloroacetonitril yields, under the same conditions, dichloroacetic acid, while trichloroacetonitril is resolved into carbon dioxide and chloroform. Potash acts in a similar way (Bucknits u. Otto, *ibid.* ix. 1591).

Di-iodonitracetoneitril, $\text{C}^2\text{I}_2(\text{NO}^2)\text{N} = \text{CI}^2(\text{NO}^2)\text{CN}$, is formed by adding iodine in small successive portions to mercuric fulminate suspended in ether, till the fulminate can no longer be detected amongst the red mercuric iodide produced by the reaction. The filtered liquid left to evaporate yields di-iodonitracetoneitril, which may be freed from admixed mercuric iodide by repeated crystallisation from the smallest possible quantity of ether, and from free iodine by quickly washing the triturated crystalline mass with very dilute soda-ley.

Di-iodonitracetoneitril crystallises from ether in well-defined colourless monoclinic prisms, sometimes several millimeters long. It tuffs yellow at 70° , melts to a red liquid at 80° , and decomposes completely at 170° . When treated with *alkalis* it gives off ammonia. It is scarcely attacked by *nitric acid*. Heated with strong *sulphuric acid*, it is decomposed, with separation of iodine. With tin and *hydrochloric acid*, it first gives off hydrocyanic acid in abundance, and finally methylamine. *Hydrogen sulphide* decomposes it, with separation of sulphur (Sell u. Biedermann, *Deut. Chem. Ges. Ber.* v. 89).

ACETOPHENONE. *Phenyl-methyl Ketone*, $\text{C}^6\text{H}_5\text{CO.CH}_3$. See PHENYL-KETONES.

ACETOPHENONIC ALCOHOL. *Secondary Phenyl-ethyl Alcohol*, $\text{C}^6\text{H}_5\text{CH}(\text{OH}).\text{CH}_3$. See PHENYL ALCOHOLS.

ACETOPHENONINE, $\text{C}^6\text{H}_5\text{N}$ or $\text{C}^6\text{H}_5\text{N}^2$.—A base produced by the action of dry ammonia on boiling acetophenone (2nd Suppl. 940).

ACETOSODACETATE, ETHYLIC. See ACETO-ACETIC ETHERS (p. 12).

ACETYL, $\text{C}^2\text{H}_3\text{O}$.—*Estimation in Substitution-products*.—Schiff determines the amount of acetyl in acetylated substitution-products, by heating a known quantity of the acetyl-derivative with a measured volume of normal soda-solution to 100° for several hours, adding to the cooled liquid a volume of normal sulphuric acid exactly equal to that of the normal soda-solution used, then filtering, washing the vessel and the filter with water, and determining, by means of the normal soda-solution, the quantity of acetic acid produced by the reaction. This method gives very exact results when acetic acid is the only acid formed, by the action of the caustic alkali on the acetylated compound. But when, as in the case of the products formed by the action of acetyl chloride on *santonin* acid and *santonin*, the action of the alkali gives rise also to another acid, viz., *santonin* acid in the case supposed, the result of the titration requires correction for the quantity of alkali neutralised by this other acid, which must of course be determined by a special experiment. The following statement of the results of two experiments on acetyl-santonin acid will sufficiently explain the mode of proceeding:—

3rd Supp.

D

	I.	II.
Acetyl-santonio acid, $C^4H^4(C^2H^2O)^4$, used .	0.630 gram	0.710 gram
Normal solution of caustic soda ($NaHO$, per 1000 c.c.)	40.00 c.c.	40.00 c.c.
Normal acid solution ($\frac{1}{2}H^2SO^4$) per 1000 c.c.	40.00 "	40.00 "
Santonio acid reproduced (determined by calculation)	0.543 gram	0.612 gram
Normal soda-solution required to neutralise the liquid	4.35 c.c.	4.90 c.c.
Quantity of the same to be deducted for the santonio acid	2.20 "	2.45 "
Quantity of the same equivalent to the acetic acid	2.15 "	2.45 "
C^2H^2O found	14.68 p.c.	14.85 p.c.
C^2H^2O calculated		14.05 "

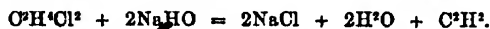
To obtain the greatest possible amount of precision, the alkaline solution may be distilled in a retort with addition of phosphoric acid, as proposed by Kissell (*Zeitschr. Anal. Chem.* viii. 933), and the acid distillate titrated with normal soda-solution. A subsequent analysis of the resulting barium salt will show whether the volatile acid produced is really acetic acid (Sestini, *Gazz. chim. ital.* iv. 454).

ACETYL-BROMIDE, CHLORIDE, &c. See ACETIC BROMIDE, CHLORIDE, &c. (pp. 20, 21).

ACETYL-CARBERIN. See ACIDS, FATTY, and CARBERINS.

ACETYL-DIPHENYLAMINE, $N(C^6H^5)^2(C^2H^2O)$.—A base obtained by the action of acetyl chloride on diphenylamine (Merz a. Weith, *Deut. Chem. Ges. Ber.* v. 283).

ACETYLENE, C^2H^2 .—According to M. P. v. Wilde (*Deut. Chem. Ges. Ber.* vii. 352), this gas may be conveniently prepared by passing the vapour of ethene dichloride over heated lime, or better, soda-lime, the following reaction then taking place:—



According to Sabanejeff (*Liebig's Annalen*, clxxviii. 109), the best mode of preparation is that devised by Miasnikoff and Sawitz (*ibid.*, cxviii. 300; cxix. 184). Ethene dibromide is added drop by drop to alcoholic potash, which is heated on a water-bath. The gases which are evolved pass through a reversed condenser into another flask containing hot alcoholic potash, and from these again through another reversed condenser. After being washed with water, the acetylene is absorbed by passing it through several bottles containing a solution of cuprous chloride in ammonia. The precipitate thus obtained is then decomposed by hydrochloric acid, and the gas is washed with water and caustic potash.

Liquid and Solid Acetylene.—According to P. and A. Thénard (*Compt. rend.* lxxviii. 219), acetylene gas, exposed to the influence of the dark discharge, condenses quickly to the amount of 4 or 5 cub. cent. in a minute, the inner surface of the tube soon becoming coated with a solid film. The substance thus formed has exactly the composition of acetylene; it withstands the action of all solvents, even of fuming nitric acid. By varying the conditions of the experiment, acetylene may also be obtained in the liquid form.

Action of Hydrogen.—When 2 vols. acetylene and 4 vols. hydrogen are mixed in a tube containing platinum-black, the mixture condenses to 2 vols. of ethane: $C^2H^2 + 2H^2 = C^2H^6$ (v. Wilde, *Deut. Chem. Ges. Ber.* vii. 352).

Action of Sulphuric Acid.—Berthelot (in 1860), by agitating acetylene with strong sulphuric acid and distilling the product with water, obtained a volatile pungent-smelling liquid, which (without analysing it or examining its properties very minutely) he regarded as vinyl alcohol, $C^2H^3.OH$, isomeric with acetaldehyde and a lower homologue of allyl alcohol (1st Suppl. 66). But from recent experiments by Lagermarck a. Elketoff (*Deut. Chem. Ges. Ber.* x. 637), it appears that this liquid is not an alcohol at all, but consists mainly of crotonic aldehyde, C^4H^6O , formed by condensation of acetaldehyde, C^2H^4O , the first product of the reaction, and convertible by oxidation with silver oxide into solid crotonic acid, $C^4H^6O^2$.

Estimation in Gaseous Mixtures.—To determine the proportion of acetylene in coal gas, Blochmann (*Deut. Chem. Ges. Ber.* vii. 274) passes the gas through ammoniacal cuprous chloride, washes the precipitate thoroughly with warm dilute aqueous ammonia, dissolves it in nitric acid, evaporates, ignites, and weighs the residue of cupric oxide. By this method Koenigsberg coal-gas was found to contain

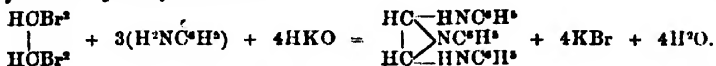
in 100 vols. 0.063 and 0.064 vols. acetylene, while that issuing from a Bunsen burner with the flame burning down gave by gasometric analysis 0.96 vol., and by determination as copper oxide 0.80 vol. acetylene.

Acetylene Bromides. The *dibromide*, $C^2H^2Br^2$, is formed in small quantity by heating an ethereal solution of the tetrabromide with mercury or finely divided silver to 180° ; also, together with a large quantity of the tetrabromide, by passing acetylene into a cold solution of 1 part bromine in 5 parts chloroform. But the only way of obtaining the dibromide in the pure state is to saturate absolute alcohol with acetylene, of which it dissolves about 6 vols., and then add the calculated quantity of bromine. By repeating this operation several times, and then adding water, the dibromide is precipitated, and may be separated from lower-boiling bye-products by heating the liquid in a salt-bath to 115° . Acetylene dibromide is a colourless, mobile liquid, which decomposes when distilled (Sabanejeff, *Liebigs Annalen*, clxxviii. 115).

Tetrabromide, $C^2H^2Br^4$ (Reboul, *Compt. rend.* liv. 1229; Sabanejeff, *Liebigs Annalen*, clxxviii. 113).—This compound is best prepared by passing acetylene gas into bromine under water; it is also formed, according to Reboul, by the action of bromine on dibromomethene, $C^2H^2Br^2$. It is a colourless aromatic oily liquid, having a sp. gr. of 2.848 at 21.5° (Sabanejeff): 2.88 at 22° (Reboul). It is insoluble in water, but dissolves in alcohol, ether, chloroform, carbon sulphide, acetic acid, and aniline. When heated to 190° it is resolved into hydrogen bromide and tribromomethene, $C^2H^2Br^3$, a liquid boiling at 162° — 163° , which is also produced by the action of ammonia on the tetrabromide, or by heating the latter with potassium acetate and acetic acid. In the preparation of the tetrabromide a small quantity of a solid modification of tribromomethene is produced, which crystallises in colourless plates sparingly soluble in alcohol and in the tetrabromide, more freely in ether and in chloroform, does not volatilise with steam, melts at 175° , and decomposes at a higher temperature (Sabanejeff).

When *sodium* is added to an ethereal solution of the tetrabromide, tribromomethene and bromoacetylene are formed, but no dibromide of acetylene; small quantities of the latter are however produced by heating the solution with silver-dust or mercury (Sabanejeff). When the tetrabromide is heated with alcoholic potash in varying proportions, only acetylene and bromoacetylene are formed, while by the action of silver acetate, potassium cyanide, and silver cyanide, no definite products could be obtained. On heating the tetrabromide with alcoholic potassium or ammonium sulphide, it is converted into a strong-smelling sulphur-compound, crystallising in transparent plates.

When an alcoholic solution of 4 mols. potash is gradually added to a mixture of 1 mol. of the tetrabromide and two of *aniline*, the chief product consists of acetylenetriphenyl-triamine:—



Part of the tetrabromide is however resolved at the same time by the action of the potash into acetylene and bromoacetylene, on which account it is best, in preparing the acetylenetriphenyltriamine, to add more bromine than would be required according to the equation above given. Other secondary reactions also take place, giving rise to glycollic acid and a body having the characters of the isocyanides (Sabanejeff).

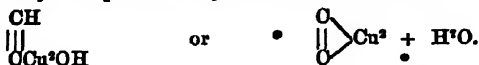
A compound isomeric with acetylene tetrabromide is formed, according to Bourgoin (*Compt. rend.* lxxix. 953), by the action of bromine on dibromosuccinic acid at 170° . On dissolving the resulting liquid in ether-alcohol, and leaving the solution to evaporate, well-defined crystals are deposited, which have the composition $C^2H^2Br^2$, melt at 54° — 55° , distil with partial decomposition at about 206° , are insoluble in water, but dissolve readily in ether, chloroform, and carbon sulphide. This compound, which Bourgoin regards as tetrabromomethene hydride (or γ -tetrabromomethane), exhibits the phenomenon of surfusion, the introduction of a crystal of the same substance into the liquid instantly determining its solidification: this phenomenon is not exhibited when a crystal of tetrabromomethene hydride is dropped into acetylene tetrabromide.

Bromoacetylene perbromide, C^2HBr^3 , obtained by the action of bromine on the perbromide of acetylene, appears to be identical in properties with the product formed by heating tetrabromomethane, $C^2H^2Br^4$, with bromine in a closed vessel; this product is almost entirely soluble in alcohol (Bourgoin, *ibid.* lxxx. 666).

When acetylene perbromide is treated with chlorine, either in direct sunshine or in diffused daylight, a chlorinated compound is formed in well-defined rectangular prismatic crystals, having only a faint taste but a strong aromatic odour. insoluble in

water, but soluble in alcohol and ether. Bourgoin (*ibid.* lxxix. 1497) assigns to this compound the formula $C^2Cl^4Br^2$, and represents its formation by the incorrect equation $C^2H^2Br^4 + Cl^4 = 2HCl + C^2Cl^4Br^2$; it should doubtless be $C^2H^2Br^4 + Cl^4 = 2HBr + C^2Cl^4Br^2$. The compound sublimes unchanged at a gentle heat, but decomposes when heated to 185° in a sealed tube into Br^2 and C^2Cl^4 . It is isomeric with perchlorethene dibromide, $C^2Cl^4Br^2$, formed by direct bromination of perchlorethene. (See CHLORETHENES, under ETHENES.)

Metallic Derivative of Acetylene.—According to Blochmann (*Deut. Chem. Ges. Ber.* vii. 274) the precipitate formed by passing acetylene into an ammoniacal solution of cuprous chloride has, when dried over calcium chloride, the composition $C^2H^2Cu^2O$, which may be represented by the structural formula :



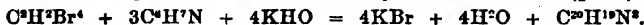
The silver-compound has, in like manner, the formula $C^2H^2Ag^2O$.

These formulæ (doubled) differ from those of Berthelot (*1st Suppl.* 35), who dried the compounds at 110° – 120° , by 1 mol. of water. These acetylides or metallo-vinyl oxides appear therefore to form hydrates in the same manner as metallic oxides; thus:—

Cupric hydrate. $Cu(OH)^2$	Cupric oxide. CuO
Argento-vinyl hydrate. $(C^2HAg^2)(OH)^2$	Argento-vinyl oxide. $(C^2HAg^2)^2O$
Cuproso-vinyl hydrate. $(C^2HCu^2)(OH)^2$	Cuproso-vinyl oxide. $(C^2HCu^2)^2O$

(Berthelot, *Bull. Soc. Chim.* [2], xxii. 441).

ACETYLENE-TRIPHENYL-TRIAMINE, $C^{20}H^{15}N^3$.—A base formed by the action of alcoholic potash and aniline on acetylene tetrabromide (p. 35):



It forms soft, silky needles, melting at 190° , and decomposing when more strongly heated; dissolves sparingly in cold alcohol, more freely in hot alcohol, and in aniline, carbon sulphide, ether, and chloroform. The hydrochloride, $C^{20}H^{15}N^3HCl$, is readily soluble in water, but insoluble in hydrochloric acid. This salt, as well as the others, decomposes slowly when its aqueous solution is left at rest, and quickly when heated, with formation of aniline. The *platinochloride*, $(C^{20}H^{15}N^3ClH)^2 + PtCl^4$, and the *mercury-compound*, $(C^{20}H^{15}N^3HCl)^4 + 3HgCl^2$, are insoluble amorphous precipitates. The bye-products obtained in preparing the triamine consist of acetylene, bromoacetylene, glycollic acid, and a compound having the smell of the isonitrils (Sabanejeff, *Liebigs Annalen*, clxxviii. 125).

ACETYLIDE. This name, originally given to the metallic derivatives of acetylene, has lately been applied by Tommasi a. Quesneville to the compound $C^2H^2O^4$, produced by the action of zinc on acetyl chloride (p. 21).

ACETYL-OXAMETHANE. See OXAMETHANE.

ACETYL-URETHANE. See URETHANE.

ACETYL-SULPHUREA. See THIO-CARBAMIDES.

ACHILLEA AGERATUM. This plant, which grows in Italy and in Provence, was formerly recommended as a remedy for worms in children, but is now cultivated only as an ornament. Its leaves when rubbed between the hands emit an odour resembling that of camphor. It contains most essence before it flowers. The essence extracted by distillation with water has the specific gravity 0.849 at 24° . It boils at 165° – 182° , the thermometer remaining stationary between 180° and 182° . This fraction, $C^2H^2O^2$, is not oxidised by contact with oxygen, even in presence of platinum-black. With acid sodium sulphite it gives a milky emulsion, which becomes clear after several days. It does not solidify at -18° . With chlorine it turns slightly reddish, and on neutralisation of the hydrochloric acid with sodium carbonate and caustic potash, a brown insoluble liquid rises to the top; and when this liquid, after distillation, is left in contact with solid potassium hydrate, the original essence is reproduced. The same result is obtained by treating the essence with bromine (S. de Luca, *J. Pharm. Chim.* [4], xviii. 105).

ACHREMATITE. A molybdo-arsenate of lead from Guanacaré, in the State of Chihuahua, Mexico. It has a compact, indistinctly crystalline structure, and a liver-brown colour, but exhibits under the microscope individual grains of sulphur-yellow

to orange and red colours. The general brown colour is due to ferric hydrate, $\text{Fe}^2\text{O}^3 \cdot \text{H}^2\text{O}$, mechanically interspersed through the mass, and incrusting the grains of the pure mineral. Streak pale cinnamon-brown. Lustre between resinous and adamantine. Translucent on thin edges; minute grains, when magnified, and clear of iron incrustation, are almost transparent. Under the polarising microscope, light fragments exhibit colours in some positions, while in others they are without action on the polarised beam; this suggests crystallisation in the dimetric or in the hexagonal system. Sp. gr. of the solid grains = 5.966; of the powder = 6.178. Hardness between that of calcspar and that of fluorspar. Fracture uneven, verging in places upon conchoidal. The mineral is easily broken and pulverised.

Before the blow-pipe it exhibits the usual characters of arsenic, molybdenum and lead. It is decomposed with difficulty by boiling with strong hydrochloric acid, and on adding water and metallic tin, a dark blue colour is gradually developed. It is imperfectly decomposed by nitric acid, and on heating it with strong sulphuric acid, adding alcohol, and cooling, a fine sapphire-blue colour is produced.

The analysis of three portions, taken from different parts of the mineral, gave, after deduction of ferric hydrate, which is merely admixed, the following results:

	(1)	(2)	(3)	Mean.
As^2O^3	18.02	17.90	18.73	18.25
MnO^2	6.19	4.87	4.98	5.01
Cl	2.14	2.08	2.24	2.15
Pb (as chloride)	6.25	6.07	6.52	6.28
PbO remaining	68.40	68.99	67.53	68.31
	100.00	100.00	100.00	100.00

These numbers agree nearly with the formula $3(\text{Pb}^2\text{As}^2\text{O}^8 \cdot \text{PbCl}^2) + 4\text{Pb}^2\text{MnO}^4$ (Mallet, *Chem. Soc. Jour.* 1876, p. 1141).

See DEXTON.

ACIDS. *State of Acids in Aqueous Solution.*—Berthelot, from his thermochemical researches on the reaction between water and acids, infers that various definite hydrates are formed in their aqueous solutions. In the case of nitric acid, for example, he finds that the curve which represents the rise of temperature on mixing the acid with water in various proportions, exhibits several points of discontinuity, indicating the existence of definite hydrates (*Compt. rend.* lxxviii. 769). According to Thomsen, on the other hand (*Deut. Chem. Ges. Ber.* vi. 697; vii. 772; *Chem. Soc. Jour.* [2], xii. 1052), this supposed discontinuity does not exist, the curve which represents the rise of temperature on mixing nitric acid, NO^3H , with water in proportions varying from 0 to 5 mols. being perfectly continuous: hence Thomsen infers that nitric acid does not form definite hydrates; and the same is the case with other acids. This conclusion is quite in accordance with the results obtained by Roscoe, who found, in the case of nitric, hydrochloric, sulphuric, formic, acetic and several other acids, that mixtures of acid and water can be formed, which boil at constant temperatures under any given pressure, but that the proportion required to produce a mixture of constant boiling-point varies with the pressure itself (*Chem. Soc. Jour.* xiii. 63; xv. 237; and this Dictionary, i. 892; ii. 687; iv. 80; 1st Suppl. 7).

Respecting the representation of the supposed hydrates of the monobasic fatty acids as atomic compounds, see Grimaux (*Bull. Soc. Chim.* [2], xviii. 535; *Chem. Soc. Jour.* [2], xi. 371) also Geuther, *Deut. Chem. Ges. Ber.* vi. 408;—also CARRERES, in this volume.

Combining Proportions of Acids and Bases.—G. Widemann (*J. pr. Chem.* [2], ix. 145) has studied the action of sulphuric acid on ferric oxide in various proportions with the view of determining the effect of varying the proportion of acid and base on the composition of the resulting salt, and the quantity of acid or base left free.

The main results of the investigation are as follows:—

(1.) If to an aqueous solution of colloid ferric oxide in a little sulphuric acid, fresh quantities of sulphuric acid are continually added, the quantity of sulphate in the solution gradually increases, while portions of the colloid oxide of iron and of the sulphuric acid remain uncombined. Even if the quantities of sulphuric acid and ferric oxide are in exactly equivalent proportions, still only about 76 per cent. of them combine, while 26 per cent. of the equivalent of acid and oxide remains free in the solution. If the quantity of sulphuric acid is less than that which corresponds with an equivalent of the dissolved oxide, the quantity of sulphate formed rises at first somewhat more quickly than that which corresponds with the increase of acid, then gradually reaches a maximum, so that half an equivalent of the acid which is added to the solution after the first, combines with about 15 per cent. more of the

equivalent of oxide, and a further half-equivalent of acid with about 4 per cent. If about four equivalents of acid are used to one of oxide, almost all the oxide enters into combination with the acid, and the maximum is so nearly reached that the difference is covered by the errors of manipulation.

(2.) Whether the oxide and acid are added in exact equivalents or in other proportions, the relative quantities of sulphate formed, and of free oxide and acid remaining, are not much affected by variations in the amount of water in the solution. Hence it follows that if the salt formed is insoluble, it will be precipitated, and part of the remaining free acid and oxide will combine, and a further precipitation will take place, and so on, till the whole of the base and acid are precipitated. In this case the original proportion of combined and free acid and base cannot be directly determined.

(3.) By addition of increasing quantities of acid to one equivalent of ferric oxide the quantity of free acid in the solution at first diminishes, till the whole quantity of (free and combined) acid in the solution amounts to somewhat more than one equivalent. On further addition of acid, the quantity of free acid in the solution increases.

(4.) If the quantity of ferric sulphate formed when one equivalent of ferric oxide is employed is divided by the equivalents of acid used, it is found that the quantity of ferric oxide combined with an equivalent quantity of acid is greatest when the quantity of acid in the solution amounts to somewhat more than one equivalent of acid to one of oxide. With larger quantities of acid, the quantity of oxide in combination with one equivalent of acid is smaller. With an infinite quantity of acid it would be infinitely small. The same proportion, however, also holds good with smaller quantities of acid, although it might be supposed that the acid would saturate itself with the excess of oxide present.

Combination of the Fatty Acids with Alkalis.—Berthelot (*Bull. Soc. Chim.* [2], xiii. 290, 307) has made experiments on the heat evolved in the formation of the alkaline salts of the first five acids of the fatty series (formic to valeric), the stability of these salts in presence of water, and their reciprocal displacements.

The quantities of heat evolved in the formation of the normal salts of these five acids with the same bases in dilute solution are nearly equal; the heat increasing slightly with the molecular weight of the acid, and varying a little with the degree of dilution.

The various isomeric acids of the butyl and amyl series disengage exactly the same amount of heat in combining with the same base, and cannot, therefore, be distinguished by this means.

In contact with water, the alkaline salts of the fatty acids exhibit a degree of stability intermediate between that of the strong acids, whose salts are not apparently decomposed by water, and those of the weak acids, such as carbonates, sulphides, and borates, which undergo partial decomposition. They approach more closely to the weak acids in proportion as their equivalent rises, from formic acid, which is almost as energetic as the mineral acids, to valeric acid, the neutral salts of which are easily changed into acid salts by evaporation, and to stearic and margaric acids, the alkaline salts of which are very easily decomposed by cold water. These salts disengage heat on dilution, especially sodium butyrate and valerate.

Influence of an Excess of Base.—All the neutral sodium salts of the fatty acids evolve an additional quantity of heat in presence of an excess of base. This heat is developed on the addition of a small quantity of base, and is probably due to the reconstitution of a neutral salt which had been previously decomposed by the water into acid and base. A further addition of base has no appreciable effect. The evolution of heat by excess of base is greater for the butyrate and valerate than for the acetate and formate, showing that the decomposition of the neutral salt increases with the molecular weight of the fatty acid present.

Influence of Excess of Acid.—The addition of an excess of acid to an alkaline salt also causes a disengagement of heat, which is especially sensible when the amount of acid added is small; and the amount of heat increases with the equivalent of the acid. The heat disengaged by the addition of an excess of acid is greater than that which is produced by a similar excess of base.

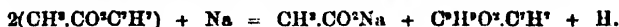
Reciprocal Displacements of the Fatty Acids.—When acetic acid is added to sodium formate, or formic acid to sodium acetate, there is a disengagement of heat which is due to the formation of acid salts. In these reactions there are two contrary thermic effects: the partial substitution of one acid for another causes an absorption of heat, and the formation of acid salts causes a disengagement of heat, and in these cases the latter preponderates. Similar results generally occur with other acids of the series, but in some cases, as in the addition of formic acid to sodium valerate, it depends

upon the proportion of acid added, whether the net result is a disengagement or an absorption of heat.

The heat of formation of the neutral salts of the fatty acids in the solid state is less than the heat evolved, under similar circumstances, with stronger acids, such as sulphuric, nitric, or oxalic acid: formic acid, being the richest in its percentage of oxygen, evolves the largest amount of heat, but, contrary to the results obtained in solution, the heat diminishes as the molecular equivalent of the acid increases, and this diminution is correlative with a diminution in the stability of the salt. (See further, *Compt. rend.* lxxi. 844; *Chem. Soc. Jour.* 1876, i. 513.)

Synthesis of Aromatised Fatty Acids. Conrad A. Hodgkinson (*Deut. Chem. Ges. Ber.* x. 254).—When benzyl acetate (300 grams) is heated to 120° with sodium (12 grams) a violent reaction takes place, attended with evolution of hydrogen. The chief products of the reaction are sodium acetate and an oily body, boiling above 300°, and giving on analysis numbers agreeing with the formula $C^{10}H^{10}O^2$. The latter product, when boiled with baryta-water, is decomposed and yields a barium salt, the acid of which agrees in composition with the formula $C^8H^8O^2$, melts at 46°, and has the characteristic properties of β -phenylpropionic or hydrocinnamic acid.

The compound $C^{10}H^{10}O^2$ is therefore the benzylic ether of hydrocinnamic acid, $C^8H^8O^2.C^2H^2$, or hydrocinnainein. It appears, therefore, that benzyl acetate is not acted upon by sodium in the same manner as the acetic ethers of the fatty series, but that the reaction takes place mainly in accordance with the equation:



Benzyl butyrate similarly treated yields the benzyl ether of phenyl-valeric acid—a liquid boiling at 240°–250° under a pressure of 120 mm. This substance is decomposed by boiling baryta-water, yielding an acid melting at 78°.

ACONITE ALKALOIDS. Beckett A. Wright (*Year-book of Pharmacy, and Pharm. Conf. Trans.* 1875) have analysed various alkaloids and their salts prepared from aconite roots, by Mr. J. B. Groves, in the following way. The ground roots were treated in a percolator with alcohol acidulated with hydrochloric acid; and the resulting extract was boiled down to a small bulk, precipitated with ammonia, and agitated with ether, whereby a mixture of bases was obtained.

Roots of *Aconitum ferox* (Nepaul aconite) thus treated yielded an ethereal extract from which a base crystallised by spontaneous evaporation; this base, called by Mr. Groves 'pseudaconitine,' yields salts so difficultly crystallisable, that hitherto they have been obtained only as varnishes. After several purifications by crystallisation from ether and alcohol, it gave numbers agreeing best with the formula, $C^{20}H^{16}NO^{11}$; the platinum salt is somewhat readily soluble in water and alcohol, and does not crystallise readily. This base is apparently the main ingredient in the preparations variously designated as 'English aconitine,' 'paraconitine,' &c.

By converting this substance into iodomercurate (by precipitation with mercuric iodide dissolved in potassium iodide), and regeneration by means of sulphuretted hydrogen (to remove mercury) and Kad acetate (to eliminate iodine) in alcoholic solution, more or less change seems to be produced. One specimen thus prepared crystallised in well-defined rhombohedrons, which showed a diminished percentage of carbon as compared with the original 'pseudaconitine;' the quantity of these crystals, however, was insufficient for the complete determination of the formula. Other specimens prepared in this way, from 'pseudaconitine' exhibited the same kind of action, the percentage of gold in the gold salt being somewhat raised, and hence apparently the molecular weight of the base being lowered; these specimens, however, did not crystallise in the well-defined rhombohedrons exhibited by the other substance. All these specimens appeared to be eminently toxic. Besides 'pseudaconitine,' amorphous or difficultly crystallisable alkaloids were obtained from the alcoholic extract; but they have not yet been fully examined.

Roots of *Aconitum Napellus* treated in the same way yielded a mixture of at least two alkaloids, forming readily crystallisable salts, besides other amorphous bases. Of these two bases, one separated partially as a hydrochloride at a certain stage during the working up of the ethereal solution; this hydrochloride, when purified by successive crystallisations, yielded numbers agreeing best with the formula, $C^{21}H^{16}NO^{11}.HCl.1\frac{1}{2}H^2O$, the formula of the free base being $C^{21}H^{14}NO^{11}$, and that of the gold salt $C^{21}H^{14}NO^{11}.HCl.AuCl^3$. The platinum salt of this base is also somewhat readily soluble. Although the salts (e.g. the nitrate and hydrochloride) of this base crystallise with great facility, it was not found practicable to obtain the free base in a crystalline form; from all solvents tried, it separated only as a varnish.

Comparatively speaking, this base is inert; its salts do not produce the tongue-prickling characteristic of aconite roots, but have a pure bitter taste.

The liquor from which this hydrochloride separated contained, besides a large quantity of the non-crystallisable base, a second alkaloid separating by spontaneous evaporation from the ethereal solution of the mixed bases in anhydrous crystals; after several crystallisations from ether, it gave numbers leading to the formula $C^{12}H^{11}NO^{12}$, the air-dry hydrochloride being $C^{12}H^{11}NO^{12} \cdot HCl \cdot 3H^2O$. This substance agrees in physiological and physical characters with the 'aconitine' of Duquesnel and others; Duquesnel, however, attributed to crystallised 'aconitine' from *A. Napellus* the formula $C^{12}H^{11}NO^{12}$ (2nd Suppl. 23), which requires numbers very different from those above given; his mode of preparation, however, was somewhat different from that adopted by Mr. Groves, alcoholic tartaric acid being employed instead of alcoholic hydrochloric acid, and the extract being evaporated at a temperature not exceeding 60° . Subjecting the alkaloid to the mercuric iodide process seems to lower its molecular weight.

It seems highly probable, on comparing the above results with those of others who have worked on the subject, that the aconite roots contain various alkaloids, or else that the alkaloid present is extremely alterable. Duquesnel has suggested that 'aconitine' is probably a glucoside; this view is quite in harmony with the results obtained, different specimens being not improbably mixtures of the glucoside and the product of its deglucosation. 'Pseudoaconitine,' when left in contact with water and emulsin, emits an unpleasant fermentative odour, and partially dissolves; the solution containing a salt which gives a reddish coloration with ferric chloride—presumably an acetate: no glucose, however, could be detected in the liquid at any stage of the action (see further Wright, *Chem. Soc. J.* 1877, i. 143).

Zinoffsky (*Chem. Centr.* 1873, 153) estimates aconitine by means of a standard solution of potassio-mercuric iodide, prepared by dissolving 13.546 grams of mercuric chloride, and 49.8 grams of potassium iodide in a litre of water. A dilute solution of aconitine in sulphuric acid is treated with alcohol, the alcohol is removed by evaporation, and the liquid treated with the standard mercuric solution prepared as above, 1 c.c. of which throws down $\frac{1}{50,000}$ of an equivalent of aconitine. The final point in the titration is determined by filtering a few drops of the liquid into a watch-glass placed on black paper, and adding one drop of the standard solution. If the reaction is complete, not the slightest turbidity will appear. The number of cubic centimeters added, multiplied by 0.02665 and increased by 0.0005, gives the amount of aconitine.

On the solubility of aconitine in chloroform, see ALKALOIDS.

ACONITIC ACID, $C^8H^6O^4$. This acid has been found by A. Behr (*Deutsch. Chem. Ges. Ber.* x. 351) in concentrated cane-juice (*Melado*) imported from the West Indies. The acid thus obtained was found to agree in composition, and in the characters of its ammonium and calcium salts, with aconitic acid prepared from citric acid, but its melting point was 172° – 173° , whereas that of aconitic acid is generally stated to be about 140° . Behr finds, however, that this latter melting point is much too low. Aconitic acid, prepared by decomposition of citric acid, was found, after purification, to melt at 168° – 169° and when still further purified, at 187° – 188° . The true melting point is difficult to determine, inasmuch as the acid in melting suffers partial decomposition.

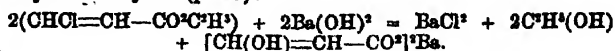
According to Pawollock (*Liebigs Annalen*, clxxviii. 160), pure aconitic acid is most readily obtained by heating 100 grams of citric acid in a small flask provided with a bent distillation-tube half a meter long, until the whole tube is coated with small oily drops. The residue is then heated in a basin on a water-bath with 15 grams of water, until it becomes solid and crystalline. On adding pure ether to the powdered mass, aconitic acid dissolves, and citric acid is left behind. Pure aconitic acid is not precipitated by boiling with lime-water, and does not prevent the precipitation of ferric oxide by ammonia, but the presence of a very small quantity of citric acid prevents it. The latter may also be detected by preparing the barium salt and examining them under the microscope, barium citrate showing very characteristic forms.

Aconitic acid combines with hypochlorous acid, but the monochloro-acid thus formed cannot be isolated, nor can its salts be obtained in the pure state, because they readily decompose, with formation of a chloride and an oxy-citrate.

ACROGENS. The wood of several of these plants, including that of a tree from Australia, has been analysed by G. W. Hawes (*Sill. Am. Jour.* [3], vii. 585), whose analyses show that it does not differ in ultimate composition from that of other trees.

ACROLACTIC ACID, $C^3H^4O^3$ = $CH(OH)=CH-CO^2H$. An acid related

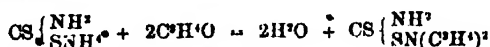
to lactic acid in the same manner as acrylic to propionic acid. Its barium salt is formed, together with barium chloride and alcohol, by the action of boiling baryta-water on ethyl chloracrylate (p. 45):



By evaporating the mixture of barium chloride and acrolactate, adding alcohol to separate the greater part of the barium chloride, then exactly precipitating the remaining barium with sulphuric acid, concentrating the filtrate on the water-bath, and finally evaporating over sulphuric acid, the acrolactic acid is obtained as a thick syrup which shows a tendency to crystallise. The silver salt, $\text{C}^2\text{H}^5\text{AgO}^2$, is white, blackens quickly on exposure to light, and is moderately soluble in water (Pinner, *Deut. Chem. Ges. Ber.* vii. 250).

• **ACROLEIN**, $\text{C}^2\text{H}^2\text{O}$. *Formation from Ethylene*.—When a mixture of ethylene with a quantity of oxygen considerably less than sufficient for its complete combustion (i.e. an equal volume or less), is exploded by the electric spark, the carbon is partly separated, partly oxidised to monoxide, while the hydrogen is set free, and a portion of the carbon monoxide thus formed unites with undecomposed ethylene, forming acrolein, $\text{C}^2\text{H}^2 + \text{CO} = \text{C}^2\text{H}^2\text{O}$. The presence of acrolein vapour in the gaseous product of the reaction may be recognised by its intensely pungent odour, and by shaking up the mixture with ether free from alcohol, which dissolves the acrolein, forming a solution which, when treated with moist silver oxide, yields silver acrylate identical in properties with that prepared from ordinary acrolein, and giving, when decomposed by sulphuric acid, the characteristic odour of acrylic acid. The formation of acrolein by the combination of ethylene and carbon oxide takes place only when the carbon oxide is in the nascent state, no such effect being produced when electric sparks are passed through a mixture of ethylene and ready-formed carbon oxide (E. von Meyer, *J. pr. Chem.* [2], x. 113).

Reactions.—1. With *Ammonium Thiocarbamate*, acrolein forms diallylidene-ammonium thiocarbamate:



(E. Mulder, *Liebig's Annalen*, clixviii. 228).

2. With *Alkaline Bisulphites*.—Hübner a. Geuther, by treating acrolein with acid sodium sulphite, obtained an uncrystallisable compound from which neither acrolein nor sulphurous acid could be produced (i. 57). Max Müller (*Deut. Chem. Ges. Ber.* vi. 1441) finds that when 1 mol. acrolein is added by small portions to a well-cooled solution of 2 mols. acid potassium sulphite, the odour of acrolein disappears entirely, but is reproduced permanently on addition of a larger quantity. The resulting liquid does not yield any crystalline product; when treated with acids, it gives off sulphur dioxide (half the amount which it contains), but no acrolein; with barium chloride, on addition of ammonia, it gives a precipitate of barium sulphite (also representing half the sulphur contained in it); and it reduces an ammoniacal solution of silver. Alcohol precipitates from it a viscid mass, softening after a while to crystalline nodules, which when dried at 140° , have a composition answering to the formula $\text{C}^2\text{H}^2\text{K}^2\text{S}^2\text{O}^2$, or $\text{C}^2\text{H}^2\text{O} \cdot 2\text{SO}^2\text{K}$. Müller designates the acid $\text{C}^2\text{H}^2\text{S}^2\text{O}^2$, corresponding with the salt, as *sulphaacrolein-sulphurous acid*, and represents its constitution by the formula $\text{CH}^2-\text{CH}(\text{SO}^2\text{H})-\text{C}(\text{OH})\text{SO}^2\text{H}$.

The potassium salt of this acid, treated with ammoniacal silver solution, yields the sulphopropionic acid, $\text{CH}^2-\text{CH}(\text{SO}^2\text{H})-\text{COOH}$, described by Buckton a. Hoffmann, and by reduction with sodium-amalgam, oxypropanesulphonic acid, $\text{C}^2\text{H}^2\text{O}(\text{OH})\text{SO}^2\text{H}$. Müller supposes that the sulphaacroleinsulphurous acid is first converted, by loss of sulphurous acid and water, into *acroleinsulphurous acid*, $\text{CH}^2-\text{CH}(\text{SO}^2\text{H})-\text{CHO}$, which then yields oxypropanesulphonic acid by reduction, and sulphopropionic acid by oxidation.

Acrolein Dimeride, $\text{C}^4\text{H}^2\text{OBr}^2$. This compound, formed by direct combination (1st *Suppl.* 58) is liquid in the first instance, but according to L. Henry (*Deut. Chem. Ges. Ber.* vii. 1112) it is converted by contact with nitric acid into a solid polymeride which crystallises from hot water in shining laminae, and by slow evaporation in well-defined prismatic crystals, melting at 59° , very slightly soluble in cold water, much more easily in warm water, and still more in alcohol. The alcoholic solution saturated with hydrochloric acid yields a body heavier than water, insoluble therein, and boiling above 200° ; it has not been analysed; but Henry regards it as probably having the composition $\text{C}^4\text{H}^2\text{Br}^2 \left\langle \begin{array}{l} \text{OCH}^2 \\ \text{Cl} \end{array} \right.$.

According to Linnemann & Penl, on the other hand (*Deutsch. Chem. Ges., Ber.* viii. 1097), the solidification of the liquid dibromide under the influence of nitric acid is by no means of constant occurrence, and, moreover, nitric acid is not essential to its production, inasmuch as the liquid compound will sometimes solidify under water, and more or less completely when simply left to itself.

The properties of solid acrolein dibromide differ to a certain extent, according to the circumstances under which the solidification has been effected. When solidified by nitric acid, it may be recrystallised from boiling benzene, but not, as stated by Henry, from water. It then forms microscopic prisms, melting at 66°. In the fused state it exhibits very remarkable properties, and decomposes with unusual facility on slight elevation of temperature. When solidified under water, the dibromide is somewhat more soluble in benzene, but crystallises in the same form, and melts at 60°. The solid dibromide changes spontaneously after some time into the liquid modification, which still retains the property of solidifying under water.

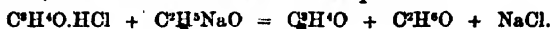
The freshly prepared liquid and the partially solidified dibromide are violently oxidised by nitric acid of sp. gr. 1.42, even at ordinary temperatures. Dilute nitric acid likewise oxidises them slowly in the cold, more quickly with the aid of heat. The perfectly solidified dibromide behaves in the same manner, dissolving slowly and with oxidation in nitric acid of sp. gr. 1.42, diluted with 2 vols. water. Henry's statement that acrolein dibromide is not oxidised by nitric acid appears, therefore, to be incorrect.

The products of the oxidation of acrolein dibromide are brominated organic acids. With nitric acid of sp. gr. 1.42 added in equivalent quantity, the mixture being cooled at first and afterwards heated, the product consists of dibromopropionic acid, $C^2H^2Br^2O^2$, identical with that which is obtained from the dibromide of allyl alcohol (see PROPIONIC ACID). With excess of nitric acid, a large quantity of oxalic acid is produced, together with tribromopropionic acid, melting at 93°.

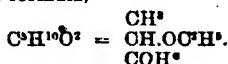
By oxidation with cold dilute nitric acid, two brominated acids are obtained, one liquid, the other crystallisable. The liquid acid dissolves sparingly in water, easily in carbon sulphide. Its sodium salt crystallises in a mass of thin silky needles, and contains an amount of bromine approximately equal to that of sodium dibromopropionate. The solid acid is insoluble in carbon sulphide, but dissolves easily in water, and may be crystallised by cooling from its solution in chloroform prepared at the boiling heat. After drying in a vacuum, it melts at 98°, and contains an amount of bromine equal to that of sodium dibromolactate (Linnemann & Penl).

Reactions of Acrolein Hydrochloride (Taubert, *Jenaische Zeitschr. f. Naturwissenschaft.* x. 1-25).—1. *With Alcoholic Sodium Ethylate*.—When acrolein hydrochloride is warmed with a slight excess of sodium ethylate, formed by dissolving 1 part of sodium in 9 parts of absolute alcohol, a violent reaction takes place; sodium chloride is separated in large quantity; and a liquid is formed, from which, by distillation with water and other processes, the following bodies have been obtained, together with some others not yet investigated:

a. *Metacrolein*, formed in accordance with the equation:



b. A body formed by the replacement of chlorine in acrolein hydrochloride by ethoxyl, and hence having the formula,



This is a colourless oily liquid, of peculiar aromatic odour, and bitter acid taste, burning with a blue non-luminous flame. It dissolves in alcohol, ether, and water. Sp. gr. 0.936 at 4°. It begins to boil at 130°, but cannot be distilled without decomposition.

c. A thick oily liquid, of yellow colour and neutral reaction, dissolving easily in alcohol and ether, but not in water, and giving, on analysis, numbers agreeing with the formula $C^2H^4O^2$. This substance is decomposed by distillation, yielding at first a large quantity of acrolein, and afterwards the compound $C^2H^4O^2$ (b) perfectly pure, whilst a black carbonised mass is left in the retort.

d. A resinous substance having the composition and properties of *hexacroleic acid*, $C^6H^{12}O^6$.

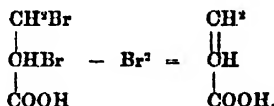
e. A body which agrees approximately with the formula, $C^3H^{12}NaO^4$, and may, therefore, be regarded as the sodium salt of a monobasic acid, $C^3H^{14}O^4$ (*triacroleic acid*), formed by the combination of 3 mols. of acrolein with 1 mol. of water.

2. *With Phosphorus Oxychloride and Trichloride.*—Acrolein hydrochloride is not attacked by phosphorus oxychloride in the cold, but when it is warmed therewith, a brisk reaction takes place, hydrogen chloride is evolved in large quantity, and the compound is carbonised, and in the end completely decomposed.

Phosphorus trichloride does not act upon acrolein hydrochloride, even when boiled with it.

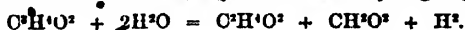
3. Acrolein hydrochloride reacts with *absolute alcohol* at 100° , with *potassium hydrate* at 140° , and with *potassium acetate* at 180° , but none of the products of these reactions have as yet been isolated.

• **ACRYLIC ACID, $C^3H^4O^2$.** This acid is formed by debromination of β -dibromopropionic acid, and may be reconverted into that acid by direct addition of bromine :



It is also converted into mono-, iodo-, bromo- and chloropropionic acids, by treatment with the corresponding haloid acids (*2nd Suppl.* 27). According to Caspary & Tollen \ddot{s} (*Ann. Ch. Pharm.* clxvii. 255), it is hydrogenised and converted into propionic acid by prolonged contact with sodium-amalgam, but not by short contact with nascent hydrogen in an acid solution. Linnemann, on the other hand (*ibid.* clxxi. 291; *Deut. Chem. Ges. Ber.* vi. 1520; vii. 854; *J. pr. Chem.* [2], x. 157), finds that when a solution of sodium acrylate is treated at the boiling heat for fifteen hours with zinc and sulphuric acid, the acid being added by successive small quantities so as to keep up a continuous gentle evolution of hydrogen, the acrylic acid is completely converted into propionic acid. The same reaction takes place, though more slowly, at ordinary temperatures.

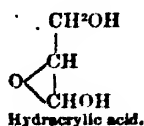
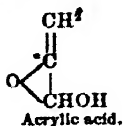
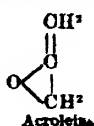
It is commonly stated that acrylic acid, when oxidised by fusion with potash, is converted into acetic and formic acids, with evolution of hydrogen (*1st Suppl.* 41):



According to Linnemann, however, this is not the case. When pure sodium acrylate was fused with potash, and the product distilled with sulphuric acid, not a trace of either formic or acetic acid could be detected in the distillate, which indeed contained nothing but a small quantity of unaltered acrylic acid. Neither is acetic acid produced by oxidation of acrylic acid with nitric or chromic acid.

These results accord with the conclusion previously arrived at by Linnemann (*2nd Suppl.* 718), that acrylic acid does not contain the group CH^2 ; and this conclusion is further borne out by the fact, recently observed by the same chemist (*Deut. Chem. Ges. Ber.* viii. 1095), that sodium acrylate heated to 100° in aqueous solution with caustic soda, takes up 1 mol. $NaHO$, forming disodic lactate, $C^3H^3Na^2O^3$, which is speedily resolved by the action of water into sodium hydrate and monosodic lactate: $C^3H^3Na^2O^3 + H^2O = NaHO + C^3H^3NaO^3$ (iii. 459); the monosodic lactate thus formed being however not a simple salt, but a mixture in equal proportions of the sodium salts of the isomeric compounds, hydracrylic acid and ethylene-lactic acid, neither of which contains the methyl group CH^3 .

Linnemann has further shown (*Ann. Ch. Pharm.* clxxi. 301) that acrylic acid is not formed from acrolein by oxidation with chromic acid, and that acrolein is not produced by heating a mixture of calcium acrylate and calcium formate. From this it must be inferred either that acrolein is not the true aldehyde of acrylic acid, or that the constitution of one or both of these bodies is not exactly analogous to that of the aldehydes and acids of the fatty series. It has indeed been already explained (*2nd Suppl.* 719) that acrolein, acrylic acid, and hydracrylic acid, may perhaps be represented by the following formulae:



Acrylic acid separated by the action of hydrogen sulphide at 170° on its lead salt (which may be conveniently mixed for the purpose with an equal quantity of sand),

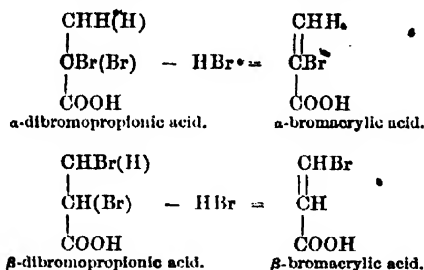
boils at about 140° , solidifies in a freezing mixture at about -15° ,* and melts at -10° . Its boiling point is therefore nearly the same as that of propionic acid, and the same relations exist between its ethers and those of propionic acid (Caspary & Tollens).

Acrylates.—*Sodium acrylate*, $C^3H^3NaO^2$, crystallises in microscopic lenticular needles, deliquescent in moist air or when placed with water under a bell jar. Its aqueous solution is nearly colourless, having only a faint yellowish tinge. A solution saturated at the boiling heat solidifies to a jelly on cooling. It is but very sparingly soluble in alcohol of 99 per cent., whether cold or hot. In alcohol of 80 per cent. it dissolves very easily, but a solution prepared at boiling heat does not crystallise on cooling. If a solution in 80 per cent. alcohol be evaporated over the water-bath till a film forms on its surface, the residual syrup after cooling solidifies immediately, on being touched, to a crystalline mass, exhibiting under the microscope groups of capillary and lenticular crystals. The salt does not alter in appearance at 250° , but at a stronger heat it gives off a little acid, then swells up and decomposes, giving off empyreumatic products. By hydriodic acid it is converted into β -iodopropionic acid (Linnemann).

The *calcium salt*, $(C^3H^3O^2)^2Ca$, is a very hygroscopic mass formed of radiate needles. The *strontium salt*, $(C^3H^3O^2)^2Sr$, forms small very soluble rhombic tablets.

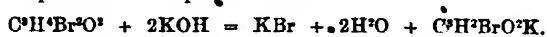
The *methyl ether*, $C^3H^3O^2.CH^3$, obtained by treating a solution of β -dibromopropionic acid in methyl alcohol with zinc and *sulphuric acid*, is a liquid having a very pungent odour, and boiling at 80° – 86° . The *allyl ether*, $C^3H^3O^2.C^3H^3$, is a liquid having a disagreeable pungent odour, and boiling between 119° and 124° . During distillation it often suddenly thickens to a jelly, the remainder then distilling over unaltered on raising the temperature. It likewise undergoes this change after a time, even at ordinary temperatures, especially in sunlight. The other acrylic ethers, as also the free acid, and several allyl-compounds, remained unaltered after exposure to sunlight for several months (Caspary & Tollens).

Bromacrylic Acid, $C^3H^3BrO^2$. Of this acid there are two modifications, α and β , formed by abstraction of HBr from α and β -dibromopropionic acids respectively:



The α -acid has been studied by Phillippi & Tollens (*Ann. Ch. Pharm.* clxxi. 333); the β -acid by Wagner & Tollens (*ibid.* 340).

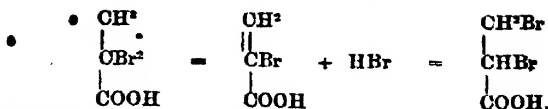
The two acids are obtained as potassium salts by the action of boiling alcoholic potash on the respective dibromopropionic acids:



α -Bromacrylic Acid.—Boiling alcoholic potash acts but slowly on α -dibromopropionic acid, and, to complete the reaction, it is necessary to use an excess of the alkali (about 3 mols. KOH to 1 mol. $C^3H^3Br^2O^2$).

Potassium α -bromacrylate crystallises from water in rhombic plates. To obtain the free acid, sulphuric acid is added to a concentrated solution of the potassium salt, and the liquid is shaken with ether. It is very soluble in water and alcohol, readily attacks the skin, and crystallises in rectangular plates melting at 69° – 70° . When kept it soon gives off hydrobromic acid, and a soft brownish mass is left behind. On heating it with 3–4 parts of fuming hydrobromic acid to 100° , it is converted into β -dibromopropionic acid, which is also produced when α -dibromopropionic acid is heated with hydrobromic acid to 100° for about a week. This striking example of a molecular change may be explained by assuming that the α -acid, which at 120° is quickly resolved into hydrobromic acid and α -bromacrylic acid, undergoes the same decomposition slowly at 100° , and thus the following reaction takes place:

* This is printed 16° in 2nd Supplement. p. 27.



β-Bromacrylic Acid.—Boiling alcoholic potash acts readily on *β*-dibromopropionic acid, and the resulting potassium bromacrylate is easily obtained pure by leaving the solution to cool until no more potassium bromide crystallises out, and crystals of the bromacrylate begin to make their appearance. The solution is then evaporated, and the residue crystallised from water, in which this salt is less soluble than the bromide. It crystallises in brilliant, rectangular, striated plates.

To prepare the free acid, a little more than the required quantity of sulphuric acid is added to a concentrated solution of the potassium salt, and the liquid shaken with a little ether, to obtain a concentrated solution, which is heavier than water, and can therefore be easily separated. On evaporating the solution, melting the residue with a little water, and pressing, the pure acid was obtained, crystallising in large brilliant square plates, or in a combination of the pyramid and prism of the first order, *P. ∞ P.* Its odour resembles that of propionic acid; it is very caustic, and blisters the skin. On distillation it undergoes partial decomposition, and when exposed to light, gives off hydrobromic acid, leaving a brownish-black syrupy mass soluble in alcohol, water, and potash. When the crystals are kept over sulphuric acid, they become white and soft, and when they are treated with water, an insoluble residue is left behind.

The *sodium-salt*, $\beta\text{-C}^3\text{H}^3\text{BrO}^2\text{Na} + \text{H}^2\text{O}$, is very soluble in water, and forms warty masses, consisting of tufts of microscopic needles.

The *ammonium-salt*, $\beta\text{-C}^3\text{H}^3\text{BrO}^2\text{NH}^4$, crystallises in plates.

The *silver-salt*, $\beta\text{-C}^3\text{H}^3\text{BrO}^2\text{Ag}$, is a crystalline precipitate, consisting of small glistening plates.

The *calcium-salt*, $\beta\text{-(C}^3\text{H}^3\text{BrO}^2)_2\text{Ca} + 4\text{H}^2\text{O}$, forms silky interwoven needles, which lose water in the air, but do not deliquesce, while the anhydrous salt when kept becomes first liquid and then changes into a brown mass.

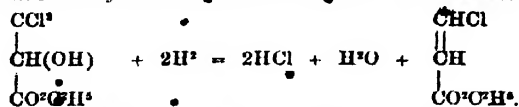
The *barium-salt*, $\beta\text{-(C}^3\text{H}^3\text{BrO}^2)_2\text{Ba} + 4\text{H}^2\text{O}$, is readily soluble in alcohol and hot water, and crystallises in microscopic rhombic plates.

The *strontium-salt*, $\beta\text{-(C}^3\text{H}^3\text{BrO}^2)_2\text{Sr}$, crystallises from alcohol in microscopic plates.

The *zinc-salt*, $\beta\text{-(C}^3\text{H}^3\text{BrO}^2)_2\text{Zn}$, is sparingly soluble in alcohol, and forms microscopic plates, often growing together in the shape of a cross.

Ethyl β-monobromacrylate could not be prepared by heating the potassium salt with alcohol and ethyl bromide; a better result was, however, obtained by using the silver-salt. It is a liquid boiling at about 155°–159°, with decomposition, ethyl bromide being formed, and a white insoluble body left behind. The acid heated with hydrobromic acid is reconverted into *β*-dibromopropionic acid, $\text{OH}^2\text{Br}-\text{CHBr}-\text{CO}^2\text{H}$.

Chloracrylic acid, $\text{C}^3\text{H}^3\text{ClO}^2$. The ethylic ether of this acid is formed by the reducing action of zinc and hydrochloric acid on ethylic trichlorolactate:—



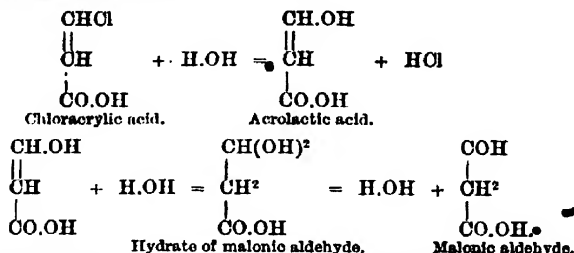
It is a limpid mobile liquid, which boils at 146°, smells like an allyl compound, and slightly attacks the eyes and mucous membranes.

This ether easily exchanges its chlorine for hydroxyl. When boiled with barium hydrate, it dissolves gradually and is converted into the barium salt of acrolactic acid, $\text{C}^3\text{H}^3\text{O}^3$, together with barium chloride and alcohol (p. 41). Boiled with alcoholic ammonia, it yields an ammoniac, together with slender needles of an *alanine*, $\text{CH(NH}^2)=\text{OH}-\text{CO}^2\text{H}$, differing from ordinary alanine, $\text{OH}^2-\text{CH(NH}^2)-\text{CO}^2\text{H}$, not only by containing 2 at. hydrogen less, but also by its structure, which is analogous to that of ethenolactic acid, $\text{CH}_2\text{(NH}^2)-\text{CH}^2-\text{CO}^2\text{H}$.

Chloracrylic ether is also formed in the reduction of trichlorolactic ether by zinc-dust and water, but a considerable portion of it is saponified by the simultaneously formed zinc-hydrate, and probably converted into zinc acrolactate. Moreover, the reduction partly goes as far as the formation of acrylic ether (Pinner, *Deut. Chem. Ges. Ber.* vii. 250).

Chloracrylic ether is partially decomposed by distillation with steam, an acid solu-

tion being formed containing *chloracrylic acid*, $C^3H^3ClO^2$. This acid is a syrup, which cannot be distilled; its salts are very soluble, and readily decompose on heating their aqueous solutions, forming metallic chlorides. On boiling the ether with baryta-water (an inverted condenser being attached), for a long time, a difficultly soluble barium salt is formed, together with small quantities of a more soluble one (probably chloracrylate or acrolactate): by means of sulphuric acid and ether the acid of the difficultly soluble salt can be extracted; it crystallises in flat prisms, melting at about 138° , and consists of malonic acid, $C^3H^2O^4$, probably formed from the chloracrylic acid by the following series of reactions:—

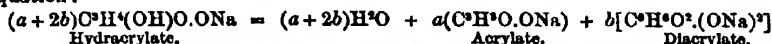


The malonic aldehyde, or homologue of glyoxylic acid thus formed, immediately oxidises to malonic acid.

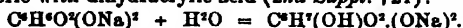
Chloracrylic ether, heated in a sealed tube with water, gives no malonic acid, gas only being formed, and scarcely any residue being left on evaporation of the resulting solution (Pinner, *Deut. Chem. Ges. Ber.* viii. 963).

Diacrylic Acid, $C^4H^3O^4 = C^4H^3O^2(OH)^2 = \begin{array}{c} C^3H^3O.OH \\ || \\ C^3H^3O.OH \end{array}$ (Wislicenus, *Liebig's*

Annalen, clxxiv. 285). This polymeride of acrylic acid is obtained as a sodium salt by the action of heat on sodium hydracrylate (2nd Suppl. 717). Wislicenus at first supposed the salt thus produced to have the same composition as sodium acrylate, and named it *paracrylate*; but subsequent experiments have led him to regard it as a mixture of acrylate and diacrylate of sodium, formed as represented by the equation:



On treating this mixture with water, it becomes very hot, and the diacrylate of sodium is converted, with assumption of water, into the sodium salt of paradipimalic acid, isomeric with dihydracrylic acid (2nd Suppl. 721):



In consequence of this tendency of the diacrylates to take up water and pass into paradipimalates, the only way of obtaining the former in the pure state is to heat them till a constant weight is obtained. A paradipimalate dried at 110° does not lose any further weight, at 150° – 160° , but at 200° – 250° it gives off water and is converted into diacrylate. Sodium diacrylate, $C^4H^3Na^2O^4$, forms an amorphous deliquescent mass which becomes perceptibly warm when breathed upon, and takes up exactly as much water (not given off at 110°) as is sufficient to convert it into paradipimalate. The barium salt, $C^4H^3BaO^4$, was prepared from the paradipimalate; the calcium salt, $C^4H^3CaO^4$, directly from the hydracrylate, by heating the latter to 220° , dissolving out the acrylate formed at the same time with water, and again heating the residue to 220° .

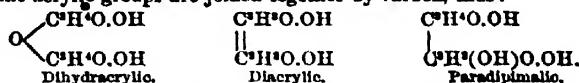
The solution obtained by treating the so-called paracrylate of sodium with water contains, therefore, nothing but acrylate and paradipimalate. On mixing it with an equal volume of absolute alcohol, the paradipimalate is thrown down as a viscid syrup while the acrylate remains dissolved. The syrupy precipitate after repeated solution in water and precipitation by alcohol hardens under absolute alcohol to such a degree as to admit of pulverisation. The sodium paradipimalate, $C^4H^3Na^2O^4 + H^2O$, prepared in this manner as by desiccation in a vacuum over sulphuric acid, dissolves in an extremely small quantity of water and is very deliquescent. At 110° it gives off its water without losing its solubility or its tendency to deliquesce. The hydrated salt is isomeric with sodium hydracrylate, $C^4H^3Na^2O^4 + H^2O = 2C^3H^3NaO^2$; and the anhydrous salt is isomeric with sodium dihydracrylate (2nd Suppl. 721), from which, however, it differs considerably in all its properties, the dihydracrylate being crystalline, non-deliquescent, not capable of taking up water of crystallisation, and dissolving somewhat freely in hot strong alcohol. Moreover, the paradipimalate is

precipitated by barium and calcium salts, whereas the dihydracrylate is not, and lastly, freedihydracrylic acid heated with hydriodic acid is converted into β -iodopropionic acid, whereas paradipimalic acid is converted by the same treatment into parapipic acid.

Barium Paradipimalate, $C^8H^8BaO^4$, forms a precipitate, gummy at first, afterwards hardening, insoluble in water. The *cupric salt*, $C^8H^8CuO^4 + H^2O$, forms blue green, compact, easily pulverisable lumps, and gives off its water at 110° . The *lead salt* is thrown down by lead acetate, as a flocculent precipitate, which dissolves only in a large excess of the precipitant, does not melt in boiling water, and cannot be recrystallised from the lead acetate solution, whereby it is essentially distinguished from the isomeric lead salt of adipimalic acid (2nd Suppl. 29); when dried in a vacuum it has the composition $C^8H^8PbO^4$.

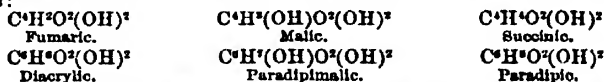
Free paradipimalic acid, probably $C^8H^8O^4$, prepared by decomposing the lead or copper salt with hydrogen sulphide and concentrating the filtrate, is a gummy mass which deliquesces in moist air.

Paradipimalic acid is also formed, as already stated (2nd Suppl. 721), as a by-product in the preparation of hydracrylic acid by the action of moist silver oxide on β -iodopropionic acid. The presence of water in this reaction likewise gives rise to the production of dihydracrylic acid from nascent acrylic acid groups, so that in dihydracrylic acid these groups must be supposed to be linked together by oxygen, whereas in diacrylic acid and paradipimalic acid (as shown by its decomposition by hydriodic acid) the acrylic groups are joined together by carbon, thus:



Paradipic acid, $C^8H^{10}O^4$, is formed by heating the syrupy solution of paradipimalic acid to 170° , in a sealed tube with hydriodic acid saturated at 10° . Its zinc salt, dried in the exsiccator, has the composition $C^8H^8ZnO^4 + 3H^2O$, and becomes anhydrous at 110° .

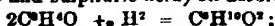
Paradipic acid, isomeric with adipic acid, is perhaps identical with the acid which is obtained, together with the latter, by the action of silver oxide on β -iodopropionic acid. The reduction of paradipimalic to paradipic acid is exactly analogous to that of malic to succinic acid, and diacrylic acid is related to paradipimalic and paradipic acids in the same manner as fumaric and maleic acids are related to malic and succinic acids:



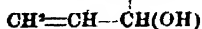
ACRYLIC COLLOIDS. These are insoluble gelatinous substances formed as secondary products during the preparation and transformation of the bromacrylic acids.

1. In the preparation of β -bromacrylic acid, especially in one operation with considerable quantities of material, a violent reaction set in, and a yellow gelatinous substance was formed. This acryl colloid leaves on drying only a small residue, resembling gelatin; it is insoluble in alcohol, ether, and water, with which it forms a bulky gelatinous mass from which mineral acids precipitate white flakes. Potash colours it yellowish; bromine and iodine do not act upon it; ammonia dissolves it almost completely, and this solution is not precipitated by hydrochloric acid.—2. A similar body is formed by keeping β -bromacrylic acid over sulphuric acid; it forms a porous mass, which differs from the first compound by being precipitated by hydrochloric acid from an ammoniacal solution.—3. A third colloid was obtained by acting with ethyl bromide on the potassium salt of the β -acid. It is insoluble in ammonia, and forms with it a yellow jelly. These three bodies have the empirical formula, $C^8H^8O^4$, and seem to be related to vegetable mucilage (Wagner & Tollens, *Liebig's Annalen*, lxxi. 355).

ACRYLIC PINACONE, $C^8H^{10}O^2$. This compound is formed by the action nascent hydrogen (from zinc and sulphuric acid) on acrolein (1st Suppl. 56):—



and its constitution may perhaps be represented by the formula:



which is that of a diatomic secondary glycol (L. Henry, *J. pr. Chem.* [2], ix. 477).

ADIPOCERE. According to Ebert (*Deut. Chem. Ges. Ber.* viii. 775), this substance consists mainly of a mixture of fatty acids, not in the form of glycerides. On treating it with potash, about 1 per cent. of ammonia was given off, and an insoluble residue (about 6 per cent.) was left, consisting of tissues, etc., and a mixture of potassium salts was obtained, which, by fractional precipitation with magnesium acetate, etc., yielded chiefly palmitic acid, $C^{16}H^{32}O_2$, with a much smaller quantity of margaric acid, $C^{17}H^{34}O_2$, hitherto known only as a synthetical product (iii. 351). The margaric acid from adipocere melts at 59° ; Heintz's synthetical margaric acid melts at 58.9° .

The last fraction, precipitable by lead acetate, but no longer by magnesium acetate, yielded oxymargaric acid, $C^{17}H^{34}O_3$, crystallising in colourless shining laminae, melting at 80° , soluble in alcohol and ether, insoluble in water, forming a white amorphous silver salt not affected by light but decomposing at 100° , and a magnesium salt easily soluble in alcohol, and crystallising therefrom in hard granules. Oleic acid was not detected.

AFFINITY. On the relations between Affinity and Dissected or Structural Formulæ, see Wright (*Phil. Mag.* [4], xlviii. 401; *Chem. Soc. J.* [2], xiii. 228).

AGARIC. See FUNGI.

AGRICOLITE. This name is given to an arsenite of bismuth, hitherto called *ahlestitite* (2nd Suppl. 120), occurring, together with eulytin, at Schneeberg in Saxony, in concentrically fibrous spherules made up of monoclinic crystals. When heated it gives off a little water and a considerable quantity of arsenious oxide, which sublimes in octahedrons. The residue dissolves easily in hydrochloric acid, leaving a small quantity of quartz. The mineral gave by analysis 57.15 per cent. bismuth oxide, 12.50 ferric phosphate, and (by difference) 30.35 arsenious oxide (Frenzel, *Jahrbuch f. Mineralogie*, 1873, 785).

AIR-BATH. An air-bath of constant temperature between 100° and 200° is described by H. Sprengel (*Chem. Soc. J.* [2], xi. 458); an improved air-bath for heating sealed tubes by J. Habermann (*Liebigs Annalen*, clxxii. 9; *Chem. Soc. J.* [2], xii. 1066).

AIR-BATTERY, Gladstone a. Tribe's. See ELECTRICITY (2nd Suppl. 448).

AIR PUMP. On Water Air-pumps for Filtration, see Mendelejeff, Kirpitschhoff a. Schmidt (*Ann. Ch. Pharm.* clxv. 63; *Jagr. ibid.* clxvi. 208); Thorpe (*Phil. Mag.* [4], xlv. 249); F. A. Wolff (*Dingl. pol. J.* ccc. 305).

On the amount of exhaustion obtainable by Sprengel's Mercurial Air-pump, see Donkin (*Chem. News*. xxix. 125; *Chem. Soc. J.* [2], xii. 537).

ALACREATINE, $C^4H^7N^3O^2$. A base isomeric with creatine, produced by direct combination of alanine with cyanamide (2nd Suppl. 393).

ALACREATININE, $C^4H^7N^3O$, formed by dehydration of alacreatine by the action of heat or acids, crystallises from water in long prisms containing 1 mol. H^2O , which it loses in dry air or when heated to 100° . With zinc chloride it forms a soluble crystallisable compound, having the composition $(C^4H^7N^3O)^2ZnCl^2$. When boiled with baryta-water it splits up into urea and alanine. It reduces mercuric oxide, forming guanidine (Baumano, *Deut. Chem. Ges. Ber.* vi. 1371).

ALAN-GILAN. The commercial name of the essential oil of *Unona odoratissima*. See UNONA.

ALANINE, $C^3H^7NO^2$. In the preparation of this substance by Strecker's method (i. 63), potassium cyanide may be used instead of prussic acid. When this is the case, the mother-liquor remaining after the alanine has crystallised out contains several substances, amongst which is lactyl-urea (2nd Suppl. 723).

ALBITE. A moonstone variety of albite from Delaware Co., Pennsylvania, is described by A. R. Leeds (*Sill. Ann. J.* [3], vi. 22). Its analysis gave:

SiO^2	Al^2O^3	Fe^2O^3	CaO	MgO	Na^2O	K^2O	H^2O
67.70	19.98	trace	1.47	0.11	8.86	1.36	0.08 = 99.56.

On albite crystals in volcanic rocks, see G. vom Rath (*Jahrb. f. Mineralogie*, 1874, 423).

On the relations of albite to other triclinic feldspars, see 2nd Suppl. p. 510.

ALBUMIN. See PROTEIDS.

ALCOHOL. See ETHYL ALCOHOL.

ALCOHOLATES. On the action of these bodies on Amides, see AMIDES.

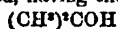
ALCOHOL-RADICLES. *Diagnosis of Primary, Secondary, and Tertiary Alcohol-radicles by means of Colour reactions.*—These different orders of alcohol-radicles may be distinguished from one another by their different behaviour with nitrolic acids and pseudonitrols. If it is required, for instance, to decide whether an iodide of the series $C^xH^{2x+1}I$ contains a primary, secondary, or tertiary alcohol-radicle, it is distilled with silver nitrite, and the distillate is treated with potash and nitrous acid. If a red colour is produced (formation of a nitrolic acid) the substance certainly contains a primary compound; if the colour is blue, it just as certainly contains a secondary compound; absence of colour indicates a tertiary compound (Meyer a. Locher, *Deut. Chem. Ges. Ber.* vii. 1510).

On the compounds of Thallium with Alcohol-radicles, see THALLIUM.

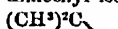
ALCOHOLS. *Formation.*—Several alcohols of the fatty series are formed in the manufacture of starch. Vauquelin showed that common alcohol is formed in the preparation of starch from wheat. Bouchardat, by distilling 120 litres of the sour water from starch-works, obtained 490 grams of a mixture of the alcohols and acetates of ethyl, propyl, and butyl. The presence of these alcohols was proved by oxidation, by which, as no acetone was formed, it was also shown that no pseudo-propyl alcohol was present. The quantity of propyl alcohol was a little more than one-third of the whole. Neither the mixture nor any of the different fractions obtained by distillation were optically active (*Compt. rend.* lxxviii. 1145).

The action of zinc on a mixture of ethyl iodide and ethyl formate gives rise to an amyl alcohol, which is probably diethyl carbinol. This mode of synthesis may perhaps be generalised (Wagner a. Saytzeff, *Deut. Chem. Ges. Ber.* vi. 1542).

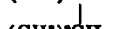
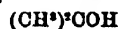
Tertiary alcohols may be formed, according to Friedel a. Silva (*Compt. rend.* lxxvi. 226), by the action of nascent hydrogen on compounds analogous in constitution to pinacolin. By adding sodium to pinacolin floating on water, a hexyl alcohol is obtained, having the constitution of dimethyl-isopropyl carbinol:



Pinacone.

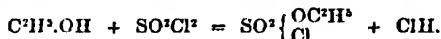


Pinacolin.



Dimethyl-isopropyl carbinol.

Action of Sulphuryl Chloride on Alcohols (P. Behrend, *Deut. Chem. Ges. Ber.* ix. 1334-1338). When 1. mol. ethyl alcohol is added, drop by drop, to 1 mol. well-cooled sulphuryl chloride, a brisk reaction sets in, and ethylsulphuric chloride is formed:—



It is a colourless oily liquid, having a very pungent smell. If, on the other hand, sulphuryl chloride be added by drops to alcohol, neutral ethyl sulphate, $SO^2(OC^2H^5)_2$, is formed as well as ethylsulphuric chloride, and ethyl chloride is given off, resulting from the action of hydrochloric acid formed in the reaction, on the excess of alcohol.

By acting on the ethylsulphuric chloride with methyl alcohol, the mixed ether, $SO^2(CH^3)(C^2H^5)$, is obtained, as a yellowish neutral liquid, which water resolves into methyl alcohol and ethylsulphuric acid.

Sulphuryl chloride acts very violently on methyl alcohol; the chloride, $SO^2(OCH^3)Cl$, thus formed, resembles the ethyl compound, but is more easily decomposed by water. On acting upon it with ethyl alcohol, a mixed sulphate is obtained, identical with that described above, and yielding with water, ethylsulphuric acid and methyl alcohol.

Butylsulphuric acid chloride, $SO^2(OC^4H^9)Cl$, formed in like manner, is, when freshly prepared, a colourless liquid, soon becoming brown and viscous. The compound obtained by the action of sulphuryl chloride on benzyl alcohol is very unstable.

Reciprocal Action of Oxalic Acid and the Monatomic Alcohols (Cahours, and Demarcay, *Compt. rend.* lxxviii. 688). The reciprocal action of dry oxalic acid and the primary alcohols of the series $C^xH^{2x+2}O$, gives rise to oxalic and formic ethers. This occurs also with the primary alcohols of the allylic series $C^xH^{2x}O$, since allyl alcohol, by similar treatment, yields a mixture of oxalo- and formio-allylic ethers.

Benzyl alcohol is likewise completely etherified, yielding an oxalate which is solid and crystallisable; it boils at a very high temperature, and is changed by ammonia into oxamide, while benzyl alcohol is regenerated.

When oxalic acid acts upon a mixture of propyl and pseudopropyl alcohols, propyl oxalate is almost exclusively formed, and if this is saponified, a mixture of the alcohols rich in normal propyl alcohol is obtained, which, when again etherified

by oxalic acid, yields nearly pure propyl oxalate. This reaction affords a method of separating the two alcohols.

On the Action of Oxalic Acid on Polyatomic Alcohols, see OXALINS.

Compounds of Alcohols with Aromatic Hydrocarbons.—Alcohols mixed with hydrocarbons and treated with sulphuric acid yield condensation-products. Allyl alcohol and benzene yield uncrystallisable hydrocarbons boiling at a high temperature, and the same alcohol, with mesitylene, yields an oily hydrocarbon which distils at about the same temperature as mercury, and a small quantity of a solid hydrocarbon which crystallises from acetone. Ethyl alcohol and methyl alcohol yield with benzene small quantities of hydrocarbons (Baeyer, *Deut. Chem. Ges. Ber.* vi. 220).

ALDEHYDE, CH^3COH . *Reactions.*—1. A mixture of aldehyde vapour and hydrogen heated in a glass tube over mercury to a temperature a little below dull redness gave, besides unaltered aldehyde, a mixture of carbon monoxide and marsh gas, whilst about one-sixth of the aldehyde had disappeared, probably in the form of condensation-products (Berthelot, *Compt. rend.* lxxix. 1100).

2. Aldehyde and zinc-ethyl act on one another, even at ordinary temperatures, and more quickly at a gentle heat, forming a crystalline organo-zinc compound; and on decomposing this with water, and heating the resulting oily liquid with moist silver oxide, methyl-ethyl-carbinol, $\text{CH}^3\text{—CHOH—C}^2\text{H}^5$, is obtained, distilling between 96° and 99° (E. Wagner, *Bull. Soc. Chim.* [2], xxv. 396).

3. When 1 part of paraldehyde is added drop by drop to 100 parts of well-cooled sulphuric acid, and the solution is shaken with a quantity of benzene rather greater than that which is required by the following equation, diphenylethane, C^6H^{10} , is produced:



The same hydrocarbon appears to be formed by mixing benzene and sulphuric acid with concentrated lactic acid, which is partially converted by the sulphuric acid into aldehyde, $\text{C}^3\text{H}^5\text{O}^2 = \text{CO}^2 + \text{H}^2\text{O} + \text{C}^2\text{H}^4\text{O}$ (Baeyer, *Deut. Chem. Ges. Ber.* vii. 1190).

In like manner a mixture of benzene and chloral or bromal treated with sulphuric acid yields diphenyltrichloroethane, $\text{CCl}^3\text{CH}(\text{C}^6\text{H}^5)_2$, or diphenyltribromoethane, $\text{CBr}^3\text{CH}(\text{C}^6\text{H}^5)_2$; and a mixture of paraldehyde, toluene, and sulphuric acid yields ditolyl-ethane, $\text{CH}^3\text{—CH}(\text{C}^6\text{H}^4\text{CH}^3)_2$.

4. *Action of Chlorine on Aldehyde.*—Krümer u. Pinner, by passing chlorine into aldehyde, cooled at first but heated to 100° towards the end of the reaction, obtained a body which they regarded as trichlorocrotonic aldehyde or crotonic chloral, $\text{C}^3\text{H}^3\text{Cl}^3\text{O}$, the chlorine being supposed first to take hydrogen from the aldehyde to form hydrochloric acid, which then exerted on the aldehyde a condensing and dehydrating action, resulting in the formation of crotonic aldehyde, which latter was converted by the excess of chlorine into crotonic chloral (2nd Suppl. 35).

This reaction has been further studied by Pinner (*Liebigs Annalen.* clxxix. 21; *Deut. Chem. Ges. Ber.* vii. 1321, 1561), who finds that when chlorine is passed into ordinary aldehyde cooled to -10° by a mixture of ice and salt, the first effect is to polymerise the aldehyde, converting it into metaldehyde and paraldehyde, which are then further acted on by the chlorine so as to form substitution-products, as above. Now paraldehyde being less volatile than ordinary aldehyde and less violently acted on by chemical reagents, is better adapted than ordinary aldehyde for the preparation of substitution-products, as it does not require to be cooled by a freezing mixture; in fact, when chlorine dried by bubbling through oil of vitriol is passed, slowly at first, into paraldehyde kept cool by immersing the containing vessel in cold water, the gas is completely absorbed, and the aldehyde is converted into a substitution-product, which, however, is not crotonic chloral, as formerly supposed, but, according to Pinner's latest experiments, butyric chloral, $\text{C}^4\text{H}^7\text{Cl}^1\text{O}$.

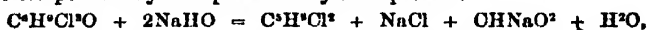
With aqueous aldehyde, the chief product is ordinary chloral, the condensation of the aldehyde to butyric aldehyde taking place only in presence of concentrated hydrochloric acid. The same result is obtained when pounded marble is added to neutralise the hydrochloric acid as fast as it is formed (2nd Suppl. 35).

When large quantities of aldehyde are subjected at once to the action of chlorine, the first portions of butyric chloral which pass over on distillation have a very pungent odour, arising from the presence of less highly chlorinated products of butyric aldehyde, and towards the end of the distillation the oily distillate no longer crystallises. The pungent-smelling oil just mentioned is produced in especial abundance when aldehyde containing alcohol is used, and it then contains products resulting from the chlorination of the alcohol. When dehydrated by calcium chloride and distilled, this oil passes over between 40° and 190° , and by repeated fractional distillation it may be separated into the following portions:—

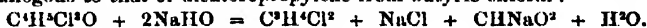
- 28—36°. Unaltered aldehyde.
 50—65°. Ethidene chloride.
 72—74°. Ethyl acetate, arising from oxidation of the alcohol, and constituting about a fourth of the entire oil.
 95—100°. Chloral, mixed with dichloraldehyde.
 100—140°. Products of no fixed boiling point.
 140—150°. Monochlorobutyric aldehyde, C^3H^3ClO , mixed with more highly chlorinated products.
 155—165°. Chiefly butyric chloral.

The portion boiling at higher temperatures than butyric chloral was several times distilled with steam, the last portions only being each time collected. The liquid thus obtained gave by analysis numbers agreeing approximately with the formula $C^3H^3Cl^2O$. By decomposing the fraction boiling between 160° and 190° with sodium hydrate, dichloropropylene, $C^3H^3Cl^2$, boiling at 78·5°, was obtained, together with dichloroacetal, $C^2H^2Cl^2O$, boiling at 183°—184°.

The heavy non-solidifying oil which passes over, as above mentioned, in the distillation of crude butyric chloral, has been obtained in small quantity only; it boils between 215° and 220°, has a slightly pungent odour, is insoluble in water, is decomposed by caustic soda, and gives by analysis numbers agreeing approximately with the formula $C^3H^3Cl^2O$. (Chlorine by experiment 49·3 per cent.; by calculation, 52·33; hence the product appears to have been contaminated with a less highly chlorinated compound.) On decomposing it with soda-ley and distilling, an oil passed over, boiling at 146°—148°, and having the composition $C^3H^3Cl^2$. The formation of this latter compound may be represented by the equation:

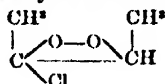
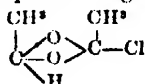


and is analogous to that of dichloropropylene from butyric chloral:



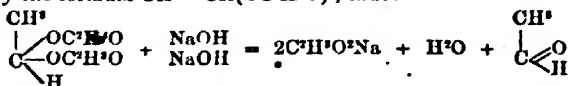
The chloride, $C^3H^3Cl^2$, possesses the sweetish odour of organic chlorides in general, and readily takes up a molecule of bromine, forming the compound $C^3H^3Cl^2Br^2$, which boils between 230° and 240°. The formula of the compound $C^3H^3Cl^2O$ and its derivatives must not, however, be regarded as definitely established.

Compound of Aldehyde with Acetyl Chloride, $C^2H^2O.C^2H^2OCl$.—This compound was discovered by Wurtz, who obtained it, together with other products, by the action of chlorine on aldehyde, and Maxwell Simpson afterwards prepared it by direct addition of acetyl chloride to aldehyde (i. 108). Wurtz (*Zeitschr. f. Chem.* 1871, 362) suggests that its composition might be represented by one of the two formulæ:



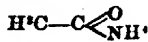
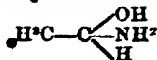
while Erlenmeyer (*Lehrb. d. Org. Chemie*) suggests for it the formula $CH^3-C \begin{array}{l} \diagup OC^2H^2O \\ \diagdown Cl \\ H \end{array}$;

and Schiff (*Deut. Chem. Ges. Ber.* ix, 364) has lately demonstrated the correctness of the latter formula by treating the compound dissolved in absolute alcohol with an equivalent quantity of potassium acetate, whereby the chlorine is precipitated in the form of potassium chloride, and replaced by an atom of oxacetyl, $(C^2H^2O^2)$; and on subjecting the liquid product to fractional distillation, a liquid is obtained boiling at 163°—168°, and agreeing in composition and properties with the ethylidene diacetate which Geuther obtained by the combination of aldehyde with acetic anhydride (i. 108). Now this last compound, when heated with a solution of caustic alkali, is resolved into 2 mols. acetate and 1 mol. aldehyde, and must therefore have the constitution represented by the formula $CH^3-CH(OC^2H^2O)^2$, thus:—



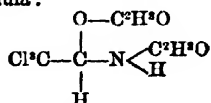
Hence also it follows that the compound of aldehyde with acetyl chloride must have the constitution suggested by Erlenmeyer.

Aldehyde-ammonia, $CH^3 \cdot O \cdot NH^2$. The constitution of this compound might be represented by either of the formulæ:

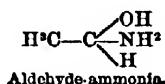
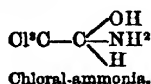


To decide between them, R. Schiff (*Deut. Chem. Ges. Ber.* x, 165) has examined the reaction of the analogous compound, chloral-ammonia, $C^2HCl^1O.NH^3$, with acetyl chloride and acetic anhydride. When either of these substances is poured upon chloral-ammonia, the mixture becomes hot, and a clear solution is formed which, on cooling or on addition of water, solidifies to a white crystalline mass. This product crystallises from water in fine rhombic tables which melt at 156° and dissolve in alcohol but not in ether. Its composition agrees with that of monoacetyl-chloral-ammonia, $C^2H^2(C^2H^3O)Cl^1ON$. Heated with acetyl chloride in sealed tubes to 120° it yields a clear solution, which on cooling deposits a white crystalline mass, soluble in ether and in glacial acetic acid, and crystallising from the latter in large transparent prisms melting at 117° – 118° .

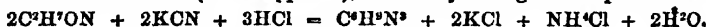
This last compound is diacetyl-chloral-ammonia, $C^2H^2(C^2H^3O)^2Cl^1ON$. It is instantly decomposed by hot water into acetic acid, which dissolves, and mono-chloracetyl-chloral-ammonia, which is deposited. Hence it appears that the two acetyl-groups in this body have different functions, the second having evidently taken the place of hydrogen in a hydroxyl-group, the presence of which in chloral-ammonia is thereby demonstrated. The constitution of the dichloracetyl-compound must therefore be represented by the formula:



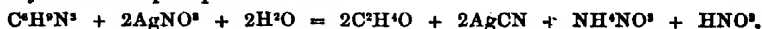
and consequently the structure of chloral-ammonia and its analogue aldehyde-ammonia by the following formulae:



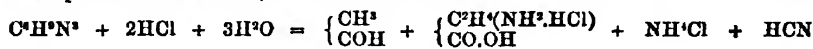
Action of Hydrocyanic Acid on Aldehyde-ammonia.—The product obtained by treating aldehyde-ammonia with nascent hydrocyanic acid (potassium cyanide and hydrochloric acid) is not a compound analogous to the diacetone-cyanhydrin formed in like manner from acetone (*2nd. Suppl.* 15), but a body having the composition $C^2H^3N^3$:



It crystallises in white needles melting at 67° – 68° . On addition of silver nitrate to the aqueous solution, silver cyanide separates, and at the same time the odour of aldehyde becomes perceptible:—



On heating it with acids, aldehyde and hydrocyanic acid are separated; if the heating takes place in sealed tubes, alanine is also obtained:—



(Ureth, *Deut. Chem. Ges. Ber.* vi, 1113).

On the reaction of Aldehyde-ammonia with Thiocyanic Ethers, see THIOCYANIC ETHERS.

Aldehyde Sulphites (H. Bunte, *Liebig's Annalen*, clxx, 305). These compounds are readily formed by dissolving aldehyde in a concentrated solution of an acid sulphite; the solution becomes hot, and remains clear after cooling, but deposits crystals when evaporated over sulphuric acid. The potassium salt, $C^2H^3SO^3K = CH^3-CH \begin{array}{l} \swarrow OH \\ \searrow SO^3K \end{array}$, forms hard, indistinct crystals, consisting of tufts of microscopic needles. The dry salt, as well as its solution, is decomposed when heated to 100° .

The sodium salt, $C^2H^3SO^3Na + H^2O$, has similar properties; it is very soluble in water, and crystallises by slow evaporation over sulphuric acid in nacreous plates; alcohol precipitates it in needles having a satiny lustre.

By mixing acid ammonium sulphite with aldehyde small needles are obtained, consisting, not of the acid ammonium salt, $C^2H^3SO^3(NH^3)$, but of an amide, $C^2H^3 \begin{array}{l} \swarrow OH \\ \searrow SO^3NH^3 \end{array}$ differing therefrom by 1 mol. H^2O . Redtenbacher (*Ann. Ch. Pharm.* lxx, 37), by passing sulphur dioxide into an alcoholic solution of aldehyde-ammonia, obtained an isomeric compound, which also forms small needles, dissolves in less than 1.5 parts of water, and when heated to 100° for forty-eight hours loses 78 per

cent., leaving a brown resin,—whereas its isomeride requires a little more than 6 parts of water for solution, and when heated to 100° loses only a few milligrams, and acquires a very faint yellow colour. Petersen (*ibid.* cii. 317) obtained a similar body by the action of sulphur dioxide on deliquesced aldehyde-ammonia; it is stable at 100° , less soluble than Redtenbacher's compound, and probably identical with that described by Bunte. Two other bodies having the same composition are known, viz., taurine, and the *isotaurine* which Kind obtained by heating the silver salt of chloroethylsulphonic acid with strong aqueous ammonia (*J. pr. Chem.* [2], ii. 222).

The barium salt cannot be prepared by direct combination, because there is no acid sulphate of barium; neither can it be obtained by adding a barium salt to a solution of one of the above compounds, because it is very soluble. To prepare it, aldehyde is added to an aqueous solution of sulphurous acid, which dissolves it with evolution of heat. By neutralising with baryta and adding alcohol, indistinct silky scales are precipitated, consisting of $(C^2H^3SO)^2Ba$. The same salt is formed by suspending barium carbonate in water, passing sulphur dioxide into it, and adding aldehyde from time to time. Its aqueous solution is decomposed at 100° , or by the action of baryta-water or sodium carbonate, but not by carbon dioxide or sulphur dioxide. On exposure to the air, it becomes turbid, from formation of barium sulphate.

Bromaldehydes. The action of bromine on aldehyde has been examined by A. Pinner (*Deut. Chem. Ges. Ber.* vii. 1490; *Liebig's Annalen*, clxxix. 67), with results identical in great part with those of former observers (i. 666; *2nd Suppl.* 36).

Aldehyde in its ordinary state is attacked by bromine with extraordinary violence; but with paraldehyde, if diluted, especially with acetic ether, the action goes on quietly. The product varies with the proportion of bromine used, but is in every case a substitution-product of acetic, not of butyric aldehyde. Hitherto only dibromaldehyde and tribromaldehyde have been obtained in the pure state, the monobrominated derivative being apparently destroyed for the most part by the hydrobromic acid formed in the course of the reaction.

Dibromaldehyde, $CHBr_2 \cdot CHO$, is the chief product obtained when 2 mols. of bromine act on 1 mol. of aldehyde. In the pure state it is a colourless liquid, boiling at 140° – 142° , with a smell resembling that of bromal. When heated strongly with water, it dissolves and forms a hydrate, $C^2H^3Br_2O + H^2O$, which crystallises in needles. If left for a long time in contact with excess of water, this compound is converted into paradibromaldehyde, $3C^2H^3Br_2O$. Pure dibromaldehyde after some time also undergoes this change. Dibromaldehyde combines easily with hydrocyanic acid to form an addition-product, $C^2H^3Br_2O \cdot HCN$, which consists of a thick syrupy oil, gradually passing into dibromolactic acid, $C^2H^3Br_2O^2$, when boiled with moderately strong hydrochloric acid. Dibromaldehyde exerts a very powerful caustic action on the skin.

Tribromaldehyde or **Bromal**, $CBBr_3 \cdot CHO$, is obtained by the action of 3 mols. of bromine on 1 of aldehyde. When mixed with water it solidifies in thin rhombic plates, whereas dibromaldehyde forms long needles. Bromal combines easily with hydrocyanic acid to form bromal hydrocyanide, $C^2HBr_3O \cdot HCN$, which remains liquid for a long time after the removal of the water and excess of acid, but solidifies at once on addition of strong hydrochloric acid, in which it is only slightly

lactic acid, $C^2H^3Br_2O^2$, in the form of a slightly coloured thick liquid having a sweet taste.

Dichloraldehyde, $C^2H^2Cl^2O$. The dichloraldehyde formed by treating dichloroacetal with about five times its weight of cold sulphuric acid, thickens in a short time to a semi-fluid mass, containing, besides ordinary dichloraldehyde, a small quantity of the amorphous polymeric modification described by Paternò (*1st Suppl.* 76), together with a second polymericide. This modification, called *paradichloraldehyde*, is easily obtained pure by washing out the thickened mass with water, and then with dilute alcohol, dissolving in a little hot alcohol, and recrystallising. It may also be produced by leaving ordinary dichloraldehyde in contact with sulphuric acid; but if a small quantity of hydrochloric acid is present, no trace of paradichloraldehyde is obtained.

Paradichloraldehyde crystallises from alcohol in large, often very perfect and regular hexagonal pyramids, having a sp. gr. of 1.69. The angles of the lateral edges = $78^{\circ} 40'$. The crystals are easily soluble in hot, much less so in cold alcohol.

They are also soluble in ether, hydrocarbons, and acetic acid.* Boiling water dissolves only traces, and microscopical crystals of the same form separate on cooling. The melting point lies between 129° and 130°. The melted mass solidifies on cooling in large crystals. At 210°–220° it sublimes, with formation of a small trace of ordinary dichloraldehyde. A quick and complete change into the liquid modification takes place between 240° and 245°, but concentrated sulphuric acid produces the change at 120°–130°. Paradichloraldehyde dissolved in carbon tetrachloride is slowly attacked by chlorine at ordinary temperatures, under the influence of direct sunlight, trichloroacetyl chloride being the chief product of the reaction. Phosphorus pentachloride acts only at a temperature which would of itself produce the change into ordinary dichloraldehyde. It dissolves with the greatest facility in anhydrous acetic acid, especially when warmed, and separates out again unchanged (Jacobsen, *Deut. Chem. Ges. Ber.* viii. 87).

ALDEHYDES. On the action of Aldehydes on Ammonium Thiocarbamate, see **THIOCARBAMATES**; for their action on Naphthylamine Bisulphite, see **NAPHTHYLAMINE** (2nd Suppl. 845).

On the compounds of Aldehydes with Aromatic Hydrocarbons, see **FORMALDEHYDE** (2nd Suppl. 533).

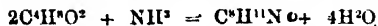
On the compounds of Aldehydes with Urethanes, see **CARBAMATES**.

ALEURITES. On the fruit of *Aleurites triloba*, called 'Candle-nuts' or 'Bancoul nuts,' see 2nd Suppl. 239; further, Corenwinder (*Compt. rend.* lxxx. 43; *Chem. Soc. Jour.* 1876, i. 97).

ALDOL. $C^4H^8O^2 = CH^3.CH(OH).CH^2.CHO$. This compound, polymeric with common aldehyde, is the aldehyde of butene-glycol, and of β -oxybutyric acid (2nd Suppl. 37). When left to itself for some weeks, it deposits crystals which may be separated from the remaining fluid portion by washing with ether. The solid body thus formed is paralldol, a polymeride of aldol, related to it in the same manner as paraldehyde to aldehyde. It softens at 80°; distils in a vacuum between 90° and 100°; dissolves easily in water and in alcohol (1 pt. in 3.8 pts. of alcohol of 99°), and crystallises from the alcoholic solution in triclinic prisms. It dissolves in 20 parts of ether at 22°, and crystallises from the solution, but the last portions of the mother-liquor contain aldol. By silver oxide it is transformed, like aldol itself, into β -oxybutyric acid (Wurtz, *Compt. rend.* lxxxiii. 255).

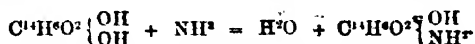
Dialdane $C^6H^{10}O^2 = 2C^3H^5O^2 - H^2O$ or $CH^3.CH(OH).CH^2.CH=CH.CH(OH).CH^2.CHO$. This substance, related to aldol in the same manner as crotonaldehyde to acetaldehyde, is formed in like manner by condensation of 2 mols. of aldol with elimination of 1 mol. H^2O , under the influence of hydrochloric acid. Dialdane melts at 139°, and distils at 137°, under a pressure of 2 centimeters of mercury. It dissolves in boiling water, but crystallises out in great part on cooling in brilliant scales. It is very soluble in alcohol, but only slightly so in ether. Its aqueous solution reduces silver oxide with formation of a mirror, giving rise to a monobasic acid, $C^6H^{10}O^4$, the silver, sodium, barium, and calcium salts of which are crystalline. This acid is formed from dialdane by the transformation of the aldehyde group, CHO , into carboxyl, $COOH$. It is strongly acid, and distils at 198° under a pressure of 2 centimeters of mercury. It is soluble in water and in alcohol, and separates from the hot aqueous solution in splendid monoclinic crystals melting at 80° (Wurtz, *Bull. Soc. Chim.* [2], xxiv. 100).

Action of Ammonia on Aldol.—When aldol-ammonia, $C^4H^8O^2.NH^3$ (2nd Suppl. 39), is distilled in a current of dry ammonia at 200°–300°, water* is formed and an oily liquid passes over containing various basic substances; amongst these is one which forms a platinum salt crystallising in regular octohedrons, and having the composition of collidine chloroplatinate. The following equation represents the reaction:—



The other bases have not yet been examined (Wurtz, *loc. cit.*).

ALIZARAMIDE. $C^4H^8NO^2$, and **ALIZARIMIDE.** $C^4H^7NO^2$ (Liebemann a. Troschke, *Deut. Chem. Ges. Ber.* viii. 379). When a somewhat dilute solution of pure alizarin in ammonia is heated for some hours to 150° or 200°, or for a long time at 100°, it is converted into *alizaramide* or *alidoxyanthraquinone*, $C^4H^8NO^2$, or $C^4H^7NO^2$ $\left\{ \begin{smallmatrix} OH \\ NH^2 \end{smallmatrix} \right.$. Its formation may be represented by the equation:



To isolate this compound, the solution is acidulated, the resulting precipitate dissolved in bartha-water, and the solution again precipitated with an acid. On recrystallising

the precipitate from boiling alcohol, alizaramide is obtained in beautiful brown needles, having a metallic iridescence. It dissolves in alcohol with a yellowish-brown colour, and is easily dissolved in the cold by solutions of the alkalis and alkaline earths. It melts at about 250° – 260° , and sublimes when carefully heated. Its barium compound has the formula $(C^{14}H^9NO^3)^2Ba$.

Alizaramide, treated in hot alcoholic solution with nitrous acid, yields oxyanthraquinone, $C^{14}H^8O^3$. Dilute alkaline solutions of alizaramide are not altered by boiling, but alizarin is regenerated when alizaramide is fused with potassium hydrate. Boiling hydrochloric acid dissolves the amide easily, without decomposition, but if the two are heated together to 250° , pure alizarin is produced, which fills the tube with long orange-red needles.

Alizarimide, $C^{14}H^9NO^3 = C^{14}H^8O^3.NH$.—If, instead of a clear ammoniacal solution of alizarin, a comparatively large quantity of flocculent precipitated alizarin is heated with strong ammonia, another product is obtained which separates in the tube in a crystalline state, whilst the alizaramide formed at the same time remains in solution. This substance is an ammonium-compound, as it gives off ammonia when boiled with a dilute solution of sodium hydrate. By digestion with dilute hydrochloric acid the ammonia is removed, and alizarimide is left. Its crystalline form is very similar to that of alizaramide, but it is scarcely soluble in ammonia, or in cold dilute alkaline solutions. With baryta-water it gives an insoluble dark violet precipitate.

ALIZARIN. See DIOXYANTHRAQUINONE, under ANTHRAQUINONE.

ALKALOIDS. *Detection.*—The following method for the detection of alkaloids in organic mixtures is recommended by Selmi (*Gazzetta chimica italiana*, iv. 1), as easier than those of Stas, Otto, and von Usler. The organic substance is digested for some hours with alcohol and a little sulphuric acid; it is then filtered, and the residue treated again in the same way. The filtrates are somewhat evaporated, filtered again, evaporated to a syrup, and freshly prepared barium hydrate is added. After addition of anhydrous baryta and powdered glass, the whole may be reduced in the mortar to a coarse powder, shaken up with perfectly pure ether, and the filtrate digested with freshly prepared lead hydrate. By then extracting with ether, the alkaloid is obtained quite pure. (See further *Gazzetta*, vi. 32; *Chem. Soc. Jour.* 1877, i. 110.)

Reactions of Alkaloids with iodised Hydriodic Acid.—This reagent yields, with the alkaloids, characteristic compounds, which are amorphous at first, but become micro-crystalline after some time, especially if they are gently heated. They decompose rapidly on exposure to the air. Nicotine, in the state of acetate, chloride, or sulphate, gives, under the above conditions, either rhombic plates or prisms of a brownish colour. Neither the acid used for solution nor the hydriodic acid should be in great excess. Brucine, when treated in the same way, yields rose-coloured rhombic plates. If the solution of brucine is very impure, the precipitate should be heated to 50° – 60° in dilute lactic acid. The crystals deposited from this solution are yellow. Very small quantities of brucine may be detected by evaporation with bromated hydrobromic acid. A yellow precipitate falls, which, on being heated at 40° , and dried at the ordinary temperature, is violet in colour. This tint is intensified by addition of a little nitric acid, after which it changes to a rose-red and finally to a purple. Iodated hydriodic acid gives dark maroon-coloured crystals with strychnine (Selmi, *loc. cit.*)

Specific reactions of the Opium Alkaloids.—Morphine, papaverine, and codeine, give with iodised hydriodic acid, crystalline compounds, the special forms of which may be readily discerned by means of a magnifying power of 450. Precipitates are produced with narcotine, narcine and thebaine, but they are not crystalline. The reaction with morphine is the most sensitive, distinct and characteristic, crystals being obtained with a single drop of a $\frac{1}{100000}$ solution of the alkaloid (Selmi, *Gazz.* v. 255).

Reactions with Potassio-platinic Iodide and Potassio-auric Iodide.—These reagents are prepared by adding a solution of potassium iodide to one of platonic chloride or auric chloride, until the precipitate at first produced is redissolved. The platinum salt is a general reagent for the detection of alkaloids in aqueous solution, and is a specific reagent for distinguishing nicotine from conessine, and also solanine from solanidine. In acetic acid solution it gives an immediate black precipitate with nicotine, but none with conessine, whilst with solanidine it yields a wine-red precipitate, but none with solanine. The gold salt serves to distinguish nicotine from conine; with the former, when the solution is evaporated, a magnificent arborescent crystallisation is produced consisting of long slender plates, whilst with conine, oily drops

are formed without any appearance of crystallisation. In a similar manner solanine is coloured brown by the gold salt, whilst solanidine merely becomes slightly yellowish (Selmi, *Gazzetta*, v. 255).

Reactions with Auric Bromide, Sodio-aurous thiosulphate, Lead tetrachloride, and the Sulphate of Manganese Dioxide. With bromide of gold, dilute solutions of conine or cicutine ($\frac{1}{100}$) give no reaction in the cold, but become violet when heated; a solution of nicotine, under similar conditions, becomes turbid at first, but regains its transparency when gently heated; at the boiling temperature, however, it takes a bluish tinge, and reduced gold is gradually deposited. Sodio-aurous thiosulphate serves to distinguish solanine from solanidine, as it gives a precipitate with the former but not with the latter; in a similar manner it precipitates narcotine, papaverine, and thebaine, but not codeine, morphine, or narceine. With daphnine it forms a rough pellicle. Sulphate of gold precipitates all the opium alkaloids with the exception of morphine. It also gives a copious yellow precipitate with solanidine, whilst with solanine, although there is no immediate precipitate, the gold is gradually reduced and deposited in the metallic state. With nicotine it yields a permanent yellow precipitate, but it does not precipitate conine.

Lead tetrachloride serves to distinguish brucine and papaverine, with which it gives brick-red precipitates. It gives a white precipitate with delphinine, and a copious crystalline precipitate with solanine; nicotine forms a yellow precipitate, whilst conine yields none (Selmi, *loc. cit.*)

Specific reactions of Methylamine, Trimethylamine, and Propylamine.—The first two of these bases give crystalline compounds with iodised hydriodic acid, and black precipitates with potassium-auric iodide. Iodide of potassium and bismuth yields a yellow precipitate with trimethylamine, but none with the others. Auric chloride gives crystalline compounds with methylamine and trimethylamine, and is reduced by propylamine after a time. Auric sulphate produces no effect with propylamine, whilst with methylamine it gives yellow plates, and with trimethylamine ruby-red crystals (Selmi).

Reactions of Alkaloids with Ammonium Molybdate.—On mixing various alkaloids with small quantities of a recently prepared solution of ammonium molybdate (8 grains dissolved in 2 drachms of pure sulphuric acid), the following reactions are observed:

(1.) No colour at first, but a clear blue tint after some time: Quinine, cinchonine, atropine, caffeine, asparagine.

(2.) *Characteristic colours.*—Solanine, yellow. Veratrine, yellowish-green, changing to dark brown, and eventually to dark blue. Narcotine, yellowish-green. Codeine, green. Morphine, dark red, changing to purple-red, then to dark blue. Digitaline, carmine, afterwards purple-red, changing to dark blue. Aconitine, clear yellowish-brown, changing through purple-red, to dark blue. Piperine, brown-red. Brucine, brick-red (J. W. Buckingham, *Amer. J. Pharm.* 1873, 149).

With Phosphomolybdic acid.—The use of this acid (or its sodium salt) was first recommended by Sonnenschein for the precipitation of alkaloids (i. 127). Further details on the mode of precipitation, and the character of the precipitates formed in particular cases are given by Stüve (*Zeitschr. Anal. Chem.* xii: 164; *Chem. Soc. J.* [2], xii, 293). See also the several Alkaloids.

Reactions with Hydrogen Sulphide.—Hofmann, by treating strychnine in alcoholic solution with yellow ammonium sulphide, obtained a compound of that alkaloid with hydrogen trisulphide, viz. $C^{21}H^{27}N^2O^4.H^2S^3$ (1st Suppl. 372). Wiechelsaus obtained sulphur-compounds of strychnine, and likewise of brucine, by the action of hydrogen sulphide on this base in alcoholic solution.

The study of these compounds has been further pursued by E. Schmidt (*Deut. Chem. Ges. Ber.* viii. 1267), who has obtained, by the action of hydrogen sulphide on strychnine, a compound crystallising in orange-red needles, to which he assigns the formula $(C^{21}H^{27}N^2O^4).(H^2S^3)^2$, and in like manner two brucine compounds represented by the formulae $C^{22}H^{29}N^2O^4.H^2S^3$ and $C^{22}H^{29}N^2O^4.2H^2S^3$. These compounds are decomposed by mineral acids, with separation of yellow oily drops consisting of hydrogen disulphide. For detailed description, see BRUCINE and STRYCHNINE.

Similar reactions appear to take place when hydrogen sulphide is passed into the alcoholic solutions of quinine, cinchonine, quinidine, cinchonidine, morphine, codeine, thebaine, papaverine, narcotine, atropine, veratrine, conine, and nicotine, the liquid turning yellow and depositing sulphur, together with sulphuretted organic compounds, all of which however are very unstable, and have not yet been obtained in definite form. The quinine-, cinchonine-, and morphine-compounds are the only ones which separate spontaneously from their alcoholic solutions, and even in these cases the

deposits obtained appear to be mixtures of several compounds. With the weak bases, caffeine and theobromine, no similar sulphur-compounds appear to be formed.

For the formation of these sulphur-compounds of the alkaloids by the action of hydrogen sulphide, the presence of oxygen appears to be an essential condition; for, if it be excluded by passing carbonic anhydride through the apparatus, and passing the hydrogen sulphide through an alkaline solution of pyrogallie acid before admitting it into the solution of the alkaloids, the liquid neither turns yellow nor deposits any sulphur-compound. The nature of the reaction may be illustrated, in the case of strychnine, by the following equation:



When hydrogen sulphide and carbon disulphide are made to act together on an alcoholic solution of strychnine or brucine (CS² alone has no effect), yellow crystalline bodies are deposited either immediately or after some time.

Solubility of Alkaloids in Chloroform.—When alkaline solutions of strychnine, quinine, quinidine, cinchonine, caffeine, theobromine, emetine, atropine, hyoscyamine, aconitine, veratrine, physostigmine, narcotine, codeine, thebaine, nicotine, or conine are shaken up with chloroform, these alkaloids are dissolved, even in the cold. Brucine, colchicine and papaverine are also dissolved after some time. Sabadilline and narceine (the latter partially) are dissolved on application of heat. Picrotoxine is easily dissolved from acid solutions. Morphine and solanine are insoluble in chloroform. By agitating the chloroform solution of any of the above alkaloids with acidified water, the alkaloid is taken up by the acid, and may thus easily be obtained in a very pure state (J. Nowak, *Chem. Centr.* 1872, 536).

On the Action of Alkaloids on the Organic Substratum of the Animal Body, see Rosbach (*N. Rep. Pharm.* xxii. 512-544; *Chem. Soc. J.* [2], xii. 173).

On the Detection of Alkaloids in Corpses, see *Deut. Chem. Ges. Ber.* vii. 1064, 1332; *Chem. Soc. J.* [2], xiii. 192, 293.

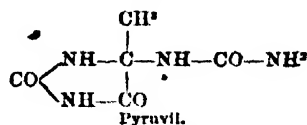
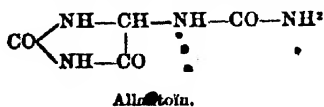
L. J. A. Cabell (*Chem. News*, xxx. 141) has analysed allanite from Amherst County, Virginia. A specimen weighing between 1 and 2 pounds presented the appearance of an imperfect crystal 3 or 4 inches long and wide, and an inch thick. The adhering matrix consisted of decomposing felspar and quartz; the colour was black; hardness between 5 and 6; sp. gr. 3.83. Analysis gave

SiO ² .	Al ² O ³ .	Fe ² O ³ .	FeO.	CaO.	LaO ² +DiO.	Y ² O.	BaO.	CaO.	MgO.	H ² O.
31.23	16.45	3.49	13.67	11.34	9.00	1.65	0.24	8.69	0.22	2.28—99.16

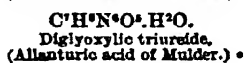
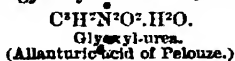
Supposing the water non-essential, and all the basic constituents, except Al²O³ and Fe²O³, to be monoxides, these numbers are nearly those of the usual formula of allanite, which is the same as that of garnet, viz. (R²R²)²Si²O¹². If, however, the cerium metals and yttrium be viewed as tri-atomic, this formula is nearly that of epidote, (R²R²)Si²O¹², to which allanite is nearly related in crystalline form.

ALLANTOÏN, C⁴H⁴N²O³. This compound is formed by heating 1 part of glyoxylic acid with 2 parts of urea to 100° for eight or ten hours. On exhausting the resulting mass with alcohol and dissolving the residue in boiling water, the solution on cooling deposits the allantoin in large shining crystals.

Allantoin may therefore be regarded as the diureide of glyoxylic acid, analogous to pyruvil, the diureide of pyruvic acid:—



The same analogy may be traced in the derivatives of these two bodies; thus:—



The allanturic acid of Pelouze was obtained by the action of hydrochloric acid on allantoin, by which reaction Mulder's allanturic acid was also formed. Similarly, pyruvil yields with strong hydrochloric acid the monureide of pyruvic acid, and with

dilute hydrochloric acid the triureide of the same acid (Grimaux, *Compt. rend.* lxxxiii. 62).

According to E. Mulder (*Deut. Chem. Ges. Ber.* viii. 1291) allantoin oxidised by potassium permanganate, in presence of free alkali, is converted into potassium allantoxanate, $C^2H^2N^2O^2K$.

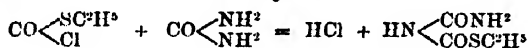
ALLOPHANIC ACID. *Ethyl Allophanate*, $C^2H^2N^2O^2.C^2H^5$.—The crystalline body, supposed to be an amidated ether, $CH(CO.NH^2)_2CO^2C^2H^5$, which Amato obtained by the action of a slightly acidulated solution of potassium cyanide on an alcoholic solution of ethyl dichloracetate (2nd Suppl. 9), has since been found to be nothing but ethyl allophanate, formed by the action of potassium cyanate contained in the crude cyanide on the alcohol used as a solvent. By treating aqueous alcohol with an acidulated solution of pure potassium cyanate, this ether may be obtained in theoretical quantity.

Fifty grams of potassium cyanate are dissolved in 300 c.c. of alcohol of 65 degrees of Gay Lussac's alcoholometer; the solution is mixed with hydrochloric acid diluted with alcohol, in sufficient quantity to produce an acid reaction; and the mixture, without separation from the crystalline powder which is deposited from it, is heated for two days in a reflux apparatus. On distilling off the alcohol and treating the residue with successive small portions of ether, nearly the whole of the allophanic ether produced by the reaction passes into solution. The crystals which separate from this ethereal solution are pressed between bibulous paper, dissolved in boiling water, recrystallised, again pressed, and dried in a vacuum.

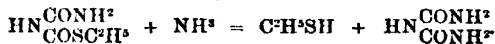
Ethyl allophanate thus prepared crystallises from water in small needles sometimes grouped in spherical masses. It is tasteless, inodorous, slightly soluble in cold water, more soluble in alcohol and ether. When heated in the air it melts and sublimates in woolly flocks. In capillary tubes it melts between 190° and 191° . Kept for some time at its melting point in a retort, it is gradually resolved into alcohol and cyanuric acid; if the ether is not quite dry, ammonia and carbon dioxide are at the same time evolved (Amato, *Gazz. chim. ital.* iii. 469).

Sulphuretted Ethyl Allophanate, $C^2H^2N^2O^2S.C^2H^5 = NH \left\{ \begin{array}{l} CONH^2 \\ COSC^2H^5 \end{array} \right.$ —

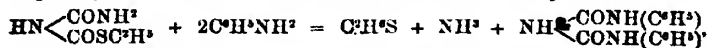
When equivalent quantities of urea and carbonyl-sulphethyl chloride (q. v.) are continuously heated to 80° – 90° in a retort with reversed condenser, the following reaction takes place:—



and after all the hydrochloric acid has escaped, there remains a white mass consisting of the sulphuretted allophanic ether. On dissolving this mass in boiling water or alcohol, filtering, and leaving the solution to cool, the ether is obtained either as a white crystalline powder, or, if the solution has been sufficiently diluted, in nacreous needles. It melts with decomposition at 180° . When continuously heated to 100° with aqueous ammonia, it yields mercaptan and biuret:—



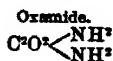
Boiled with baryta-water, it yields mercaptan and barium allophanate. The sulphuretted ether therefore behaves like ordinary allophanic ether, yielding, however, mercaptan where the latter would yield alcohol. On heating it with aniline, either directly or in alcoholic solution, the odour of mercaptan is immediately developed, and after a few seconds also that of ammonia, showing that a diphenylated product, viz., diphenyl-biuret, has been formed, according to the equation:



the reaction being precisely analogous to that by which Hofmann obtained diphenyl-biuret from ethyl allophanate and aniline (2nd Suppl. 193). The diphenyl-biuret thus obtained separated on cooling, and after repeated crystallisation from alcohol, melted at 210° (Peitzsch & Salomon, *J. pr. Chem.* [2], vii. 477).

The preceding reactions show that allophanic ether may be regarded as the amido-ether of a bibasic acid, $HN \begin{array}{c} COOH \\ \diagdown \\ COOH \end{array}$. Moreover, since allophanic ether is converted into biuret by heating with aqueous ammonia, and into diphenyl-biuret, as shown, by heating with aniline, it follows that biuret and allophanic ether stand to one another in the same relation as oxamide and oxamethane:—





(Salomon, *J. pr. Chem.* [2], ix. 290).

ALLOPHITE. This mineral, formerly regarded as serpentine, has been shown by Lefler's analysis to be a distinct species. It forms compact microcrystalline masses, penetrated by laminae of biotite. Hardness less than that of calcspar. Sp. gr. = 2.641. Pale green, more transparent than the generality of serpentines. In a thin section, under strong magnifying power, allophite appears as an aggregate of felled scales like pseudophite, the parent rock of the onstatite of the Aloysthal in Moravia, which it resembles in many respects. Its chemical composition is:—

SiO ² .	Al ² O ³ .	MgO.	Fe ² O ³ .	Cr ² O ³ .	H ² O.
36.225	21.925	35.525	2.175	0.860	2.975 = 99.675.

Neglecting the small amount of water which escapes at a high temperature, Lefler gives for allophite the formula $2(\text{Al}^2\text{O}^3.\text{SiO}^2) + 3(\text{MgO}.\text{SiO}^2)$, (Websky, *Jahrb. f. Mineralogie*, 1874, 429).

ALLOXAN and ALLOXANIC ACID. On the constitution of these bodies see Salomon, *J. pr. Chem.* [2], ix. 400; *Chem. Centr.* 1874, 451.

ALLOYS. On the Expansion and Specific Heat of Fusible Alloys (of bismuth, tin, lead, and cadmium), see W. Spring (*Ann. Chim. Phys.* [5], vii. 168; *Chem. Soc. Jour.* 1876, ii. 592).

ALLYL or DIALLYL, C³H⁵ = $\begin{array}{c} \text{CH}^2=\text{CH}-\text{CH}^2 \\ | \\ \text{CH}^2-\text{CH}-\text{CH}^2 \end{array}$. On the formation of this

hydrocarbon by heating a mixture of allyl bromide, bromobenzene, and benzene with sodium, see 2nd Suppl. p. 46.

Diallyl-dichlorhydrin, C⁶H¹²Cl²O² = $\begin{array}{c} \text{OH} \\ | \\ \text{Cl} \end{array} \text{C}^3\text{H}^5 \cdots \text{C}^3\text{H}^5 \begin{array}{c} \text{OH} \\ | \\ \text{Cl} \end{array}$, is formed by the union of diallyl with 2 mols. of hypochlorous acid, the combination easily taking place on adding the diallyl to a cooled and moderately strong solution of the acid (prepared by the action of chlorine on mercuric oxide). The mercury contained in the crude product is precipitated from this solution by hydrogen sulphide, taking care to stop the addition of that reagent as soon as the yellow precipitate of mercuric oxy-sulphide begins to turn black, as otherwise sulphuretted diallyl-compounds will be formed. The diallyl-dichlorhydrin is dissolved out by ether, the ether then distilled off, and the product dried in a vacuum over oil of vitriol.

Diallyl-dichlorhydrin is a colourless or faintly yellowish, translucent, very thick, tenacious liquid, having a very pleasant odour and a bitter caustic taste. Sp. gr. = 1.4 at 7°. It is very soluble in alcohol and ether, slightly soluble in water, remains liquid at -20°, and may be distilled without decomposition under ordinary atmospheric pressure.

ALLYL ALCOHOL and ETHERS. Linnemann has shown (*Deut. Chem. Ges. Ber.* viii. 854) that allyl alcohol treated with zinc and sulphuric acid, either at ordinary temperatures or at 100°, takes up hydrogen, and is converted into normal propyl alcohol. The allyl alcohol used in the experiments was prepared from glycerin and oxalic acid, by Tollens' method (1st Suppl. 90). It contained about 5 per cent. propyl alcohol, for the removal of which it was converted into the dibromide, C³H⁵OBr², which was then reduced by zinc and water. The allyl alcohol thus purified still retained 1.6 per cent. of propyl alcohol; but after treatment with zinc and sulphuric acid at 100° it was found to contain 11 per cent., and after similar treatment at the ordinary temperature, 34 per cent. of propyl alcohol. The statement of Tollens (1st Suppl. 91), that allyl alcohol is not converted into propyl alcohol by the action of nascent hydrogen in acid solution, is thus disproved. The same transformation is effected, but much more slowly, by the action of nascent hydrogen evolved in an alkaline solution from water and sodium-amalgam (Linnemann).

No pseudopropyl alcohol, or acetone, is formed by the hydrogenation of allyl alcohol, or by oxidation of the products of the reaction.

Constitution of Allyl Alcohol and Ethers.—Allyl cyanide, C³H³.CN, has the constitution represented by the formula CH²=CH=CH.CN, inasmuch as it is converted by oxidation into crotonic acid, CH³-CH=CH-COOH. On the other hand, allyl alcohol is known to have the constitutional formula CH²=CH-CH²OH. Hence it follows that when allyl alcohol is converted into crotonic acid through the medium of the iodide and cyanide, a change of structure must take place at some stage of the process, viz., either in the conversion of the alcohol into the iodide, which would then

be not $\text{CH}^2=\text{CH}-\text{CH}^2\text{I}$, but $\text{CH}^2-\text{CH}=\text{CHI}$, or in that of the iodide into the cyanide (2nd Suppl. 396). That the change of structure cannot take place in the passage from alcohol to iodide is shown however by the fact that the allyl alcohol regenerated from allyl oxalate (prepared with the iodide obtained from pure allyl alcohol from glycerin), is absolutely identical with the alcohol employed in the preparation of the oxalate. Further, it is found that when allyl alcohol or allyl iodide is oxidised with nitric or chromic acid, both yield formic acid by addition of oxygen to the group CH^2 , together with oxalic or carbonic acid, but no acetic acid, whereas allyl cyanide, when similarly treated, readily yields acetic acid, by addition of 2 at. oxygen to the group CH^2-CH . Hence it appears that the change of structure takes place in the conversion of the iodide into the cyanide (Kekulé & Rinné, *Deut. Chem. Ges. Ber.* vi. 386).

Occurrence of Allyl Alcohol in Wood-Spirit.—According to Aronheim (*Deut. Chem. Ges. Ber.* vii. 1381), the pungent smell of crude wood-spirit is due to the presence of allyl alcohol. The liquid fractionally distilled and rectified over lime yields the hydrate boiling at $88^\circ-89^\circ$ described by Tollens, and from it the anhydrous alcohol boiling at $96^\circ-97^\circ$ may be obtained.

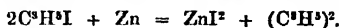
Allyl Alcohol Dibromide, $\text{C}^3\text{H}^4\text{Br}^2\text{O}$.—In the preparation of this compound for the purification of allyl alcohol as above described, it was found that two modifications were obtained, differing greatly in solubility, one dissolving in 34 times its bulk of water at 15° , the other in 3 or 4 times its bulk (Linnemann).

Compound of Allyl Alcohol with Chloral.—These bodies unite in equal numbers of molecules, forming the compound $\text{CCl}^3.\text{CH}(\text{OH})(\text{OC}^3\text{H}^4)$, which is a viscid liquid, colourless when fresh, but gradually becoming coloured on exposure to the air. It boils at 116° , and solidifies in a freezing mixture to needles melting at 20.5° ; dissolves slowly and with decomposition in water; and unites with 1 mol. of bromine, forming a syrupy yellow liquid, probably $\text{CCl}^3.\text{CH} \begin{smallmatrix} \text{OH} \\ \text{OCH}^2\text{CHBr}.\text{CH}^2\text{Br} \end{smallmatrix}$, which solidifies at low temperatures to a vitreous mass, and cannot be distilled. It is violently attacked by phosphorus pentachloride, and after decomposition of the phosphorus oxychloride by water, a colourless liquid is obtained, boiling with decomposition at 195° , agreeing in its amount of chlorine with the formula $\text{CCl}^3.\text{CHClO}.\text{C}^3\text{H}^4$, and capable of uniting with bromine (Ogilby, *Gazz. chim. ital.* iv. 463).

A compound of allyl alcohol with ethyl cyanide, $\text{C}^3\text{H}^4\text{CN}.\text{C}^2\text{H}^5\text{O}$, and a compound of allyl cyanide with ethyl alcohol, $\text{C}^3\text{H}^4\text{CN}.\text{C}^2\text{H}^5\text{O}$, are described in the 2nd Suppl. p. 49.

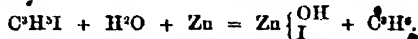
Allyl Cyanocarbons, $\text{CO} \begin{smallmatrix} \text{CN} \\ \text{OC}^3\text{H}^4 \end{smallmatrix}$ (*ibid.* 415).

Allyl Iodide, $\text{C}^3\text{H}^4\text{I}$.—This ether is but slowly acted on by a dry copper-zinc couple at ordinary temperatures, but at 100° the action is moderately rapid, the greater part of the iodide being split up in such a manner as to yield zinc iodide and diallyl:



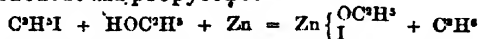
About a fifth part of the diallyl however is dehydrogenised, in a manner not clearly understood, and at the same time polymerised, yielding a resinous substance having the composition $n\text{C}^3\text{H}^4$. No satisfactory evidence of the formation of zinc-allyl has been obtained, even when the reaction takes place in presence of ether.

In presence of water, allyl iodide is easily decomposed by the couple at ordinary temperatures, yielding zinc iodohydroxide and propylene:



Zinc alone has little or no action on the iodide in presence of water.

In presence of alcohol the action of the couple on allyl iodide is too violent to yield definite results, and even with zinc alone it is necessary to keep down the temperature. The reaction succeeds best with alcohol of sp. gr. 0.805, the products being zinc iodethoxide and propylene:



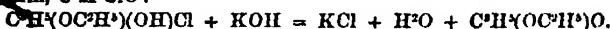
(Gladstone & Tribe, *Chem. Soc. J.* [2], xii. 208).

Products obtained by the action of Hypochlorous and Hypobromous Acids on Allyl derivatives.—The allyl compounds, having two of their carbon atoms doubly linked, as represented by the formula $\text{CH}^2=\text{CH}-\text{CH}^2\text{X}$, are capable of taking up a molecule of ClOH or BrOH , the double linking being thereby broken up and a compound produced, represented by the general formula $\begin{smallmatrix} \text{Cl} \\ \text{or Br} \end{smallmatrix} \text{H}^2\text{C}-\text{CH}(\text{OH})-\text{CH}^2\text{X}$.

To prepare these bodies, the allyl alcohol or ether is shaken up in a stoppered flask with dilute hypochlorous or hypobromous acid (prepared by the action of chlorine or bromine on mercuric oxide suspended in water), care being taken to prevent too great a rise of temperature. When no further evolution of heat is observed on addition of a fresh portion of the acid, the liquid is left to cool, shaken up with ether, and left to evaporate; the product of the combination then remains behind.

Allyl Alcohol and Hypochlorous Acid unite to form ordinary glyceric monochlorhydrin, $C^3H^5(OH)Cl$ or $CH^2Cl-CH(OH)-CH^2OH$, a colourless limpid liquid having a faint smell and taste, and easily soluble in water. Sp. gr. = 1.40 at 13° ; b. p. $230^\circ-235^\circ$; vapour-density 4.15; calc. 3.81; (compare i. 893).

Allyl-ethyl-ether and Hypochlorous Acid yield glyceric monochloroethylin, $C^3H^5(OC^2H^5)(OH)Cl$, a colourless somewhat thick liquid having a fruity smell and sharp taste, sp. gr. = 1.117 at 11° ; b. p. $183^\circ-185^\circ$; vapour density = 4.3; calc. 4.7. It is soluble in water, though less so than monochlorhydrin, and behaves in general like an alcohol, being converted by phosphorus pentachloride into $C^3H^5(OC^2H^5)Cl_2$; by the pentabromide into $C^3H^5(OC^2H^5)CBr_2$; by acetyl chloride into $C^3H^5(OC^2H^5)(OC^2H^3O)Cl$; by strong nitric acid into $C^3H^5(OC^2H^5)Cl(NO_2)$; and by alkalis into ethyl-glycide, $C^3H^5(OC^2H^5)O$, a compound analogous in constitution to epichlorhydrin, C^3H^5ClO :



Allyl Acetate and Hypochlorous Acid unite to form monochloracetin, $C^3H^5(C^2H^3O)(OH)Cl$, a thick colourless liquid having a penetrating smell and bitter taste. Sp. gr. = 1.27 at 9° ; b. p. 230° ; vapour-density 4.87.

Allyl Bromide, $CH^2=CH-CH^2Br$, and Hypochlorous Acid, yield the chlorobromhydrin, $C^3H^5(OH)BrCl$ or $CH^2OH-CHCl-CH^2Br$; and the isomeric compound, $CH^2OH-CHBr-CH^2Cl$, is obtained by the action of hypobromous acid on allyl chloride. (See CHLOROBROMHYDRINS.)

Allyl Chloride and Hypochlorous Acid yield a dichlorhydrin, $C^3H^5Cl_2(OH)$, which has the constitution of dichlorinated normal propyl alcohol, $CH^2Cl-CHCl-CH^2OH$, and is accordingly converted by oxidation with nitric acid into dichloropropionic acid, $CH^2Cl-CHCl-COOH$. Ordinary dichlorhydrin, on the other hand (formed by heating glycerin with hydrochloric acid), is converted by oxidation into dichloroacetone, $CH^2Cl-CO-CH^2Cl$, and must therefore have the constitution of dichlorinated pseudopropyl alcohol, $CH^2Cl-CHOH-CH^2Cl$ (L. Henry, *Deut. Chem. Ges. Ber.* vii. 757; *J. pr. Chem.* [2], x. 185).

SECONDARY AND TERTIARY ALCOHOLS CONTAINING ALLYL.—**Allyl-dimethyl carbinol**, $(C^3H^5)(CH^3)_2COH$, is formed by the action of zinc on a mixture of allyl iodide and dimethyl ketone. It boils at 119° , unites with 2 at. bromine, and when treated with acetic anhydride yields an acetic ether boiling at 136° .

Methyl-diallyl Carbinol, $CH^3(C^3H^5)_2COH$, formed by the action of zinc on a mixture of allyl iodide and acetic ether; boils at 168.4° (corr.), unites with 4 at. bromine, and when treated with acetic anhydride, yields an acetic ether boiling at 177.3° (corr.) (A. Saytzeff, *Deut. Chem. Ges. Ber.* ix. 33).

Diallyl Carbinol, $(C^3H^5)_2CHOH$, is formed by the action of zinc on a mixture of allyl iodide and ethyl formate (M. Saytzeff, *Liebigs Annalen*, clix. 339).

A mixture of allyl iodide, ethyl iodide, and ethyl formate, treated with zinc, also yields, not ethyl-allyl carbinol as might be expected, but diallyl carbinol (Kanonnikoff a. A. Saytzeff, *ibid.* 338).

ALLYLACETIC ACID, $C^3H_5(C^2H^3O)_2 = CH^2=CH-CH^2-CH^2-COOH$. The formation of the ethylic ether of this acid by the action of sodium hydrate on ethylic allylacetate, has been already explained (p. 14). This ether boils at $142^\circ-144^\circ$, and when boiled with potash yields allylactic acid, as an oil which floats on water, and boils at 182° . Its potassium salt crystallises in easily soluble scales; the calcium salt in laminae having the composition $(C^3H^5O_2)_2Ca + 2H^2O$. By oxidation with chromic acid it yields succinic and formic acids, $C^3H^5O_2 + O = C^2H^3O_2 + CH^3O_2$ (F. Zeidler, *Deut. Chem. Ges. Ber.* viii. 1035).

ALLYLAMINES. 1. **Ethylallylamine**, $C^2H^5N = (C^3H^5)(CH^3)NH$ (A. Rinne, *Liebigs Annalen*, clixviii. 261).—This base, isomeric with piperidine, is prepared by the action of ethyl iodide on allylamine. The mixture of the two substances in equal numbers of molecules, which soon becomes hot, is enclosed in a well-cooled sealed tube, left to itself for a while, and then heated for a short time in the water-bath. The aqueous solution of the product is then distilled with potash-ley, the base received in hydrochloric acid, and the solution of the hydrochloride evaporated to dryness. On heating the dry residue over the water-bath with solid potassium hydrate, a strongly alkaline liquid passes over, consisting of unaltered allylamine,

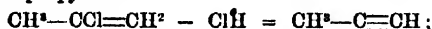
ethylallylamine, and a small quantity of diethylamine, from which, after dehydration with solid potash, the ethylallylamine, which boils at 84° , is easily separated as a colourless liquid having a strong ammoniacal odour and miscible in all proportions with water. *Ethylallylamine hydrochloride*, $C^2H^{11}N.HCl$, crystallises in small colourless plates, very soluble in water, and deliquescent on exposure to the air; less soluble in alcohol. On mixing its solution with excess of platinic chloride, evaporating, washing with a mixture of alcohol and ether, and crystallising from alcohol, the *platinochloride*, $2(C^2H^{11}N.HCl).PtCl_4$, is obtained in beautiful red monoclinic prisms. The *sulphate*, $2C^2H^{11}N.H^2SO_4$, is extremely soluble in water, but does not dissolve in alcohol or in ether. After evaporation of the solution over sulphuric acid, it forms a mass consisting of small tabular crystals.

Diethylallylamine, $C^4H^{12}N = (C^2H^5)_2(C^2H^3)N$, is formed in somewhat considerable quantity in the action of allylamine and ethyl iodide in equal numbers of molecules, and remains for the most part in the distillation-vessel when the mixture of bases is evaporated over the water-bath. On adding water to the residue, the diethylallylamine rises to the surface as an oil, and passes over with the first portions of water-vapour when the liquid is distilled over an open flame. It may be dehydrated with solid potash, and separated from a small quantity of ethyl-allylamine by fractional distillation.

Diethylallylamine is a colourless transparent liquid boiling between 100° and 103° . It dissolves in about twenty times its own volume of water, and the solution exhibits in a high degree the property—observed also in other bases, especially coneine—of acquiring, on slight rise of temperature, a milky turbidity, due to the separation of a portion of the dissolved base. *Diethylallylamine hydrochloride*, $C^4H^{12}N.HCl$, separates, on evaporating its solution over sulphuric acid, in small colourless crystals, very soluble in water. The *platinochloride*, $(C^4H^{12}N.HCl)_2.PtCl_4$, forms small reddish crystals, not very well defined.

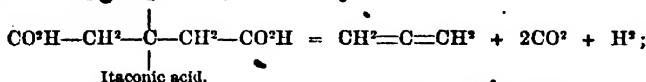
Diethylallylamine is isomeric with ethylpiperidine (iv. 657), from which it is distinguished, in the same way as ethylallylamine from piperidine, by boiling at a temperature about 25° lower (Rinne).

ALLYLENE, C^3H^4 . Of this hydrocarbon there are two modifications, α and β . α -*Allylene*, $CH^2=C=CH$, is formed by the action of alcoholic potash on mono-, chloro-, or monobromopropylene:

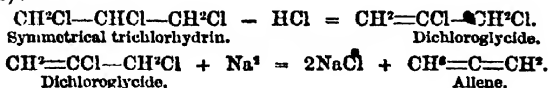


also by heating acetonic chloride, $CH^3-CCl^2-CH^3$, with sodium, and by other processes already mentioned (1st Suppl. 95). This is the modification which precipitates copper and silver solutions. It is readily dissolved by strong sulphuric acid, forming allylenesulphonic acid, $C^3H^3SO^3H$, which yields a well-crystallised barium salt not decomposed by water. The aqueous solution of this acid, when heated, yields a distillate containing mesitylene, C^9H^{12} , a polymeride of allylene (A. Schroke, *Deut. Chem. Ges. Ber.* viii. 17).

β -*Allylene* or *Allene*, $CH^2=C=CH^2$, is formed by electrolysis of itaconic acid, being given off, together with carbon dioxide, at the positive pole, while hydrogen escapes at the negative pole:—



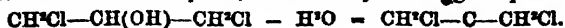
also by the action of sodium on dichloroglycide, $C^2H^2Cl^2$ (from symmetrical trichlorhydrin):



This modification does not precipitate copper and silver solutions. With bromine it forms a tetrabromide, $CH^2Br-CHBr-CH^2Br$, which crystallises in laminae.

Allene dichloride, $CH^2Cl-C-CH^2Cl$, is formed when symmetrical dichlorhydrin is

added by drops to phosphoric anhydride contained in a retort; and passes over, together with unaltered dichlorhydrin, on cautiously distilling the product:



It is a liquid having a sp. gr. of 1.233 at 17.5° , distilling at 109° , burning with a

1 with green; insoluble in water, but miscible with alcohol
2 atoms of chlorine, forming allene tetrachloride, $\text{CH}^2\text{Cl}-\text{CCl}^2-\text{CH}^2\text{Cl}$, a colourless liquid having a sp. gr. of 1.668 at 17° , a pungent turpentine-like odour and a burning taste; also with 2 at. bromine, forming the dichlorodibromide, $\text{CH}^2\text{Cl}-\text{CBr}^2-\text{CH}^2\text{Cl}$, a colourless, somewhat viscid liquid of sp. gr. 2.083 at 17.5° , boiling at 212° , and resembling the tetrachloride in taste and smell. The dichloride or its solution in benzene is decomposed by sodium, yielding free allene; and on passing this gas into bromine, the tetrabromide is formed, $\text{C}^2\text{H}_2\text{Br}_4$, which crystallises in leaflets melting at 195° (Hartenstein, *J. pr. Chem.* [2], vii. 95).

Pinner & Krämer (*Liebigs Annalen*, clviii. 37) described a dichlorallylene, $\text{C}^2\text{H}^2\text{Cl}^2$, said to be obtained by the action of alkalis on 'crotonic chloral,' $\text{C}^2\text{H}^2\text{Cl}^2\text{O}$, and this dichlorallylene was further said by Pinner (*Deut. Chem. Ges. Ber.* viii. 902) to yield, when treated with sodium, a hydrocarbon, C^2H^2 , which he called *propargylene*; but subsequent experiments have shown that this hydrocarbon really consists of C^2H^2 (one of the modifications of allene), and consequently that the supposed crotonic chloral is really butyric chloral, $\text{C}^2\text{H}^2\text{Cl}^2\text{O}$ (Pinner, *ibid.* 1561). Compare p. 60.

ALOIN (Tilden, *Pharm. J. Trans.* [3], vi. 208; *Chem. Soc. Jour.* [2], xiii. 1270). Four varieties of this substance have been distinguished, viz.: 1. *Barbaloin*, discovered by T. and H. Smith, and analysed by Stenhouse in 1851. 2. *Socaloin*, isolated from socotrine aloes by T. B. Groves, in 1856. 3. *Nataloin*, discovered by Flüchiger in 1871. 4. *Zanaloin*, prepared by Histed from a variety of socotrine aloes, imported by way of Zanzibar, analysed by Flüchiger in 1871; in all probability identical with socaloin. (For the description of Barbaloin and Nataloin, see i. 148; 1st Suppl. 99; 2nd Suppl. 52).

Zanaloin is prepared by making up the coarsely powdered aloes into a paste with proof spirit, macerating for a few hours, and then gradually expressing the liquid from the mass. The yellow cake which remains is purified by crystallisation from water, and afterwards from rectified spirit.

Zanaloin dried by exposure to the air at the ordinary summer temperature retains a quantity of water of crystallisation varying according to the state of the atmosphere. In a vacuum over sulphuric acid, it lost in two experiments 14.06 and 13.9 per cent. water, at $105^\circ-120^\circ$, the loss was somewhat greater, viz. 14.46 to 15.95 per cent. After drying in a vacuum, it gave, by three concordant analyses, 59.49 per cent. carbon, and 5.80 hydrogen, agreeing with the formula $\text{C}^{16}\text{H}^{10}\text{O}^7$.

Bromozanaloin, $\text{C}^{16}\text{H}^{10}\text{Br}^2\text{O}^7$, is easily obtained by pouring an aqueous solution of the aloin into excess of bromine water. A yellow precipitate is then thrown down which crystallises from spirit of wine. In this case, as also in the preparation of the corresponding compound from barbaloin, it is essential to the production of a pure compound to proceed in the manner indicated, as when the operation is reversed, the bromine being introduced into the aloin solution, a mixture of brominated compounds is thrown down, containing a smaller proportion of bromine, and these bodies cannot be separated by recrystallisation.

Chlorozanaloin, $\text{C}^{16}\text{H}^{10}\text{Cl}^2\text{O}^7$, is obtained by the action of hydrochloric acid and potassic chlorate. The scaly crystals are bright yellow, and lustrous, and closely resemble those of chlorobarbaloin. They contain about 14 per cent. of water of crystallisation.

Acetyl-zanaloin, $\text{C}^{16}\text{H}^{10}(\text{C}^2\text{H}^3\text{O})^2\text{O}^7$, is a pale yellowish amorphous compound, prepared by boiling the aloin with acetic anhydride, diluting the liquid with alcohol, and then pouring it into water.

Acetyl-barbaloin, prepared in the same way, is a yellowish-white curdy substance.

The following is a comparison of the analytical results obtained by different experimenters with the aloins of Barbadoes and Zanzibar aloes:—

Barbaloin (dried in a vacuum).	Bromo-Barbaloin.	Chlorobarbaloin.	Acetyl-barbaloin.
(mean).	Stenhouse (mean).	Tilden.	Tilden.
C H	C H Br	C H Cl	O H
59.31 5.8	35.48 2.78 41.97	45.17 3.70, 25.13	58.63 5.41
Zanaloin (dried in a vacuum).	Bromozanaloin.	Chlorozanaloin.	Acetyl-zanaloin.
Stenhouse (mean).	Tilden.	Tilden.	(mean).
C H	C H Br	O H Cl	C H
59.49 5.80	34.05 2.65 43.06	— — 25.04	58.84 5.38
59.2 5.9			

These numbers show that barbaloin and zanaloin have the same percentage composition. Stenhouse's numbers for bromobarbaloin are indeed somewhat different from those of Tilden, but as he prepared this compound by adding bromine-water to the aloin, it was perhaps not quite pure.

Barbaloin and zan- or socaloïn are isomeric, not identical, though they closely resemble each other in taste, solubility, and in furnishing chrysammic acid under the prolonged action of nitric acid. Zanaloin is, however, slightly paler in colour, and richer in water of crystallisation. The only qualitative test by which they can be distinguished is with nitric acid, which with barbaloin gives an instant crimson coloration, fading quickly to orange-red. Zanaloin, on the contrary, gives with the same liquid no immediate coloration, but an orange-red on the application of heat.

The numbers above given for the percentage composition of barbaloin and zanaloin, in the anhydrous state, agree with the formula $C^{16}H^{18}O^7$. Stenhouse formerly gave for barbaloin the formula $C^{17}H^{18}O^7$. According to E. Schmidt (*Deut. Chem. Ges. Ber.* viii. 1276), on the other hand, barbaloin contains 58.50 p.c. carbon, and 5.80 hydrogen, leading to the formula $C^{16}H^{16}O^7$ (calc. 58.50 C. and 5.19 H.), agreeing with the analysis of socaloïn by Sommaruga a. Egger (*Chem. Centr.* 1874, 422). The same chemist, by adding an aloin solution to excess of bromine-water, obtained a tribromaloïn, which, after several recrystallisations, gave numbers agreeing exactly with the formula $C^{15}H^{12}Br^3O^7$, together with less highly brominated compounds.

Graebe a. Liebermann, by heating aloin with zinc-dust, obtained a hydrocarbon, which they regarded as anthracene; according to Schmidt, it is methyl-anthracene, and gives by oxidation with chromic acid, anthracene-carbonic acid (m.p. 281°), together with a substance which exhibits the reactions of anthraquinone, but has no constant melting point (210°–240°); probably a mixture of anthraquinone and methyl-anthraquinone.

ALUMINIUM. *Occurrence in Plants.*—Recent exact analyses of the ashes of plants show that aluminium is not to be found among the constituents of flowering plants, and that its presence is confined to a few cryptogams. The following results have been obtained by Church (*Chemical News*, xxx. 137):

	Percentage of ash in dry plant.	100 parts of ash contain:	
		Silica.	Alumina.
Lycopodium alpinum	3.68	10.24	33.50
" clavatum	2.80	6.40	15.24
" Selago	3.20	2.53	7.29
Selaginella Martensii	11.66	41.03	0.26
" spinulosa	3.44	6.67	none.
Equisetum maximum	20.02	62.95	none.
Ophioglossum vulgatum	8.25	5.32	none.
Psilotum triquetrum	5.06	3.77	trace?

Oxidation.—Aluminium oxidises when its surface is rubbed with a piece of soft leather impregnated with mercury. The rubbed surface becomes warm and dull, and in a few seconds whitish exfoliations appear, consisting of pure alumina. The presence of the mercury appears to be necessary to produce this result (Jehn a. Hinzo, *Deut. Chem. Ges. Ber.* vii. 1498).

Action on Metallic Chlorides.—Aluminium reduces zinc as regulus from fused zinc chloride, but does not reduce magnesium chloride (Flavitzky, *ibid.* vi. 195).

On the action of Aluminium and Iodine on Ethyl Oxide and Compound Ethers, see ETHERS.

Estimation.—*Indirect estimation of Alumina in presence of Ferric Oxide.*—The two oxides are precipitated together by ammonia; the precipitate is washed, ignited, and weighed; the residue is dissolved in dilute sulphuric acid, and heated with zinc till the ferric oxide is reduced to ferrous oxide; and the latter is estimated volumetrically with permanganate. The amount of ferric oxide calculated therefrom, and deducted from the weight of the ignited precipitate, gives the alumina (MacLagan, *Chem. News*, xxix. 199).

An examination of the methods for effecting the quantitative separation of Alumina, Ferric Oxide, and Phosphoric Acid, is given by W. Flight (*Chem. Soc. Jour.* [2], xii. 592).

On the estimation of Aluminium and Iron in Phosphates, see also Esilmann (*Chem. News*, xxviii. 208; *Chem. Soc. Jour.* [2], xii. 190).

Aluminium Chloride, Al^3Cl^3 .—This compound may be prepared in the anhydrous state by converting alumina into sulphide, and then the sulphide into chloride. The alumina is heated to redness in a porcelain or earthenware tube which, as soon as all

the water is expelled from the alumina, is connected at one end with a receiver, and at the other end with a delivery-tube, by which is introduced a mixture of hydrochloric acid gas and vapour of carbon sulphide, obtained by simply passing the gas through liquid carbon sulphide. A reaction then takes place, aluminium sulphide being formed and immediately decomposed by the hydrogen chloride, yielding aluminium chloride, which distils over, mixed with sulphur and impregnated with hydrogen sulphide. This crude aluminium chloride may be purified by distilling it with iron filings. This mode of preparation does not require the use of pure alumina, as common clay will answer the purpose equally well. In that case, the silicium chloride, formed at the same time, escapes as gas, and the chlorides of iron, calcium, &c., being less volatile than the aluminium chloride, remain behind when the latter is distilled (P. Curie, *Chem. News*, xxviii. 307).

Palladiosoehloride, $\text{AlCl}_3 \cdot 2\text{PdCl}_2$.—A solution of aluminium chloride mixed with palladium chloride, deposits on concentration deep-brown monoclinic crystals easily soluble in water and in alcohol, and having the composition $\text{AlCl}_3 \cdot 2\text{PdCl}_2 + 20\text{H}_2\text{O}$. These crystals give off 16 mols. water at 140° , and the rest at a higher temperature; the compound decomposing at the same time (A. Welkow, *Deut. Chem. Ges. Ber.* vii. 802).

The **platinochloride**, $\text{AlCl}_3 \cdot 2\text{PtCl}_4$, is deposited, on evaporating a solution of the mixed chlorides, in long orange-yellow prisms containing 30 mols. of water. The crystals are triclinic, having the axis $a : b : c = 1 : 0.6418 : 0.5373$, and inclined at the angles $bc = 92^\circ : ad = 91^\circ 35' : ab = 90^\circ 50'$. Observed faces:

100 010 210 310 110 210 310 101 112 323 311

This salt is hygroscopic in moist air, very soluble in water and in alcohol, insoluble in anhydrous ether. It melts at 52° , gives off 24 mols. water at 120° , and the rest, with decomposition, at 200° . Its solution is decomposed by zinc, with liberation of hydrogen and deposition of aluminium hydrate and platinum (Wolkow, *Deut. Chem. Ges. Ber.* vii. 304).

Aluminium Nitride, AlN . This compound was obtained in an attempt to produce a compound of aluminium and carbon, by heating aluminium with sodium carbonate to a very high temperature. The product was a dark grey sintered mass, consisting of unaltered aluminium, a small quantity of carbon in a state of admixture, and small crystals of the nitride, hard enough to scratch quartz (J. W. Mallet, *Chem. Soc. Jour.* 1876, ii. 349).

Aluminium Silicates. See SILICATES.

Aluminium Sulphide, Al_2S_3 .—Experiments on the formation and properties of this compound have been made by Reichel (*J. pr. Chem.* [2], xii. 55), which, however, add but little to our previous knowledge of it, derived from the observations of Wöhler and of Frémy (i. 160). It is formed by direct combination at high temperatures, as when sulphur is added to red-hot aluminium, or when a mixture of aluminium turnings and sulphur is thrown into a red-hot crucible, the combination in both cases being attended with sparkling; also, when a stream of carbon dioxide charged with sulphur vapour is passed over ignited aluminium. It is also produced by igniting alumina in vapour of carbon sulphide, but not by heating alumina with sulphur, even in presence of a reducing agent.

Aluminium sulphide is yellow, and usually pulverulent; fuses with great difficulty, and then forms a hard crystalline mass. Heated in contact with the air, it burns to aluminium oxide and sulphurous oxide. By water or moist air it is decomposed, as represented by the equation:



ALUMES. These salts are variously formulated, accordingly as the aluminium or analogous metal contained in them is regarded as trivalent or quadrivalent; crystallised potassium alum, for example, either as $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, or as $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$. Now the atomicity of aluminium and its congeners, chromium and iron, is not yet positively determined, the arguments in support of one view or the other being for the most part based upon general considerations of analogy, while the more direct evidence which might be afforded by the vapour-density of aluminium compounds is contradictory, aluminium appearing as a tetrad when united with chlorine, bromine, and iodine, but as a triad in its methyl- and ethyl-compounds.

Further evidence bearing on this question may be derived from the number of water-molecules which the crystallised alum gives off when heated. Hartwig found (*Ann. Chem. Phys.* 1860) that crystallised potassium-alum containing $24\text{H}_2\text{O}$, gives off

the decomposition (Naumann, *Dent. Chem. Ges. Ber.*, viii. 1630; see further, *ibid.* x. 456; *Chem. Soc. J.* 1877, ii. 166).

Detection and Estimation of Alum in Flour and Bread.—According to R. J. Moffat (*Amer. Chemist* [2], i. 365), the best reagent for detecting alum in flour and bread is an alcoholic extract of Brazil wood, prepared by digesting 120 grains of the wood with 8 ounces of methyl alcohol for 18 hours, and then filtering. This liquid is coloured pale yellow or straw yellow by bread free from alum, whereas if alum is present, the colour becomes dark red. See also Davis (*Chem. News*, xxv. 207); Horsley (*ibid.* 230).

In the process given in this Dictionary (i. 660) for the quantitative estimation of alum in bread, it is recommended that, after digesting the charred bread in strong hydrochloric acid, and separating the silica from the extract in the usual way, the acid filtrate be nearly neutralised with sodium carbonate, and treated with excess of alcoholic potash, which will precipitate the phosphates of calcium and magnesium, together with a trace of iron phosphate, and leave aluminium phosphate in solution. It is found however that the separation thus effected is very imperfect, for the calcium phosphate forms a kind of jelly, which retains aluminium phosphate so obstinately that even boiling potash or soda cannot dissolve out more than a relatively small portion of it. A better mode of separation is that of A. Dupré (*Chem. News*, xxix. 233; *Chem. Soc. J.* [2], xii. 916), which consists in dissolving out the calcium and magnesium phosphates by means of acetic acid, the aluminium phosphate, together with a trace of iron phosphate, then remaining undissolved. 100 grms. of the bread (crumb only) are incinerated in a platinum dish. The ash is fused with three times its weight of pure sodium carbonate, or a mixture of potassium and sodium carbonates in equal proportions. The fused mass dissolved in hydrochloric acid is evaporated to dryness, the residue re-dissolved in acid, and the silica filtered off. To the filtrate ammonia is added to slight precipitation. The precipitate is re-dissolved by about six drops of strong hydrochloric acid. A slight excess of ammonium acetate is now added, and the mixture set aside over-night. The precipitate formed is filtered off, washed, and re-dissolved in hydrochloric acid, the solution boiled for a few minutes with a little sodium bisulphate, excess of sodium hydrate is added, and the boiling continued for a few minutes. The precipitate, chiefly magnetic oxide of iron, is filtered off, the filtrate feebly acidified with hydrochloric acid, and ammonium acetate added in slight excess. After standing all night, the precipitate, now consisting of pure aluminium phosphate, is collected on a filter, washed, dried, ignited, and weighed. Its weight in grains, multiplied by 542, gives the number of grains of alum corresponding with the amount of alumina in 2 lbs. of the bread. Instead of separating the iron as above, the two phosphates may be re-precipitated a second time with ammonium acetate, and weighed together. The iron in the precipitate is estimated by a standard bichromate solution. The amount of phosphate corresponding therewith, deducted from the total, gives the amount of aluminium phosphate. When a large proportion of magnesium phosphate is present in solution, slight traces of it are always carried down, even if in the cold. To remove this impurity, the first precipitate is to be dissolved and re-precipitated as directed. If the precipitation takes place at the boiling heat, both magnesium and calcium phosphates are partially precipitated.

For further details and modifications of this process, see Wanklyn (*Chem. News*, xxxi. 66).

A method depending on the solubility of aluminium phosphate in caustic alkalis is described by J. C. Thresh (*Pharm. J. Trans.* [3], v. 886; *Chem. Soc. J.* 1876, i. 109).

Alum from the Solfatara waters of Puzzuoli.—These waters yield by spontaneous evaporation (going on for a year) an alum crystallised in octohedrons of sp. gr. 1.774 at 17°, and exhibiting the following composition:—

SO ²	Al ² O ³	(NH ⁴) ² O	FeO	Fe ² O ³	CaO	MgO	K ² O	H ² O	X*
34.74	6.70	10.82	0.97	1.10	0.65	0.30	0.17	40.98	1.57 = 100.

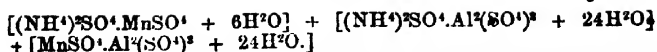
* Na²O, Mn and loss.

It is therefore essentially an ammonio-Aluminic sulphate.

The mother-liquor contained the same substances, together with a large quantity of silica, a little organic matter, and traces of chlorine (S. de Luca, *Compt. rend.* lxxiv. 123).

Capillary Alum from South Africa.—To a capillary alum from the Bosjeman River H. Ludwig (*Arch. Pharm.* [2], clxiii. 27) assigns, from analyses by himself, C. Kanoldt, A. Beyer, and Burgmeister, the complex formula:

ALUMS.

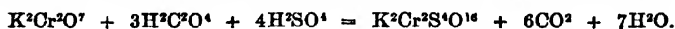


to which correspond the values given under B, those found by analysis being given under A :

	NH ⁴	MnO	Al ² O ³	SO ³	H ² O
A. (found).	1.007	7.442	10.470	35.900	46.993 = 101.812.
B. (calc.)	0.992	7.251	10.519	35.016	46.222 = 100

With traces of Fe, CaO, and MgO.

Chrome Alum.—In preparing this salt from a mixture of potassium dichromate and sulphuric acid, the reduction of the chromic acid may be conveniently effected by oxalic acid, as there is then no occasion to add an excess of the reagent, the reaction being completed when the evolution of carbonic acid ceases, and moreover the necessity of heating the mixture is avoided, which often gives rise to the formation of a green uncrystallisable solution. The reaction takes place according to the equation :



29.5 parts of the dichromate are dissolved in 39 parts of strong sulphuric acid, and the requisite quantity of water, and after cooling, 38 parts of crystallised oxalic acid are added by small portions (Lielegg, *Dingl. pol. J.* ccvii. 321).

Modifications.—The changes of this salt from the green to the violet modification and the contrary have been studied by Gernez (*Compt. rend.* lxxix. 1332), and Lecoq de Boisbaudran (*ibid.* 1491). Gernez finds that even the most concentrated solutions of the green salt, if sealed up in tubes while boiling, preserve their green colour and deposit no crystals even after several months. When such solutions are evaporated without contact of any alum crystal, they leave a residue of green transparent solid matter, which may be kept indefinitely without change. If, however, a green saturated solution, whether recently prepared or long preserved in the sealed tubes, be touched with a crystal of any alum whatever, an immediate deposit of violet octohedral crystals takes place, and the crystallisation proceeds slowly till the whole of the liquid is transformed into the violet modification. Contact of crystals of salts other than alums, potassium sulphate for example, does not induce crystallisation in the green solutions.

According to Lecoq de Boisbaudran, blue solutions of chrome alum recently prepared in the cold gradually acquire a greener tint, and green solutions recently prepared by boiling slowly become blue. Whether the liquids be dilute or concentrated, in open vessels or in closed vessels, in contact with crystals or not, they slowly approximate to the same colour. The progress of the action may be measured by the changes of volume accompanying these molecular transformations. The mode of experimenting is to place in an apparatus resembling a large thermometer one portion of a solution prepared in the cold, and in another similar apparatus some of the same solution which has been boiled; the two vessels are placed successively in baths at 15° and 30°, in order to graduate their stems, and are then allowed to assume the ordinary temperature. At the end of some hours, the blue liquid is found to have dilated, while the green solution has contracted. The curve which represents the expansion of the blue liquid shows that the action rapidly falls off in intensity and becomes gradually slower. Two such portions of a solution were found not to have acquired precisely the same tint even after the lapse of eight years.

It does not appear possible to prepare an alum containing chromic instead of sulphuric acid. E. Fleischer (*Arch. Pharm.* [3], ii. 300) endeavoured to prepare such an alum; first, by the action of barium chromate upon common alum; secondly, by means of calcium chromate; thirdly, by direct combination of aluminium chromate with potassium monochromate. All these attempts failed, in the last case because potassium monochromate decomposes neutral aluminium chromate, forming potassium bichromate and basic aluminium chromate; and, in the first two cases, because the action is very slow, and alumina is precipitated as chromate.

A further reason why such an alum cannot be formed is that chromic acid, like vanadic, tungstic, molybdic, and titanio acids, forms for the most part anhydrous salts, with which it will readily combine, giving rise not only to double, but also to multiple acid anhydrous salts.

Selenic Alums.—O. Petersson has examined the aluminio-selenic alums of potassium, sodium, and ammonium, and the chromio-selenic alums of potassium and ammonium. The potassium and ammonium salts of both groups crystallise easily; sodio-aluminic selenate less easily, on account of its greater solubility. Attempts to prepare sodio-chromic selenate and the ferri-co-selenic alums were unsuccessful (*Deut. Chem. Ges. Ber.* vi. 1466).

ALUNITE, or **ALUM-STONE** (A. v. Lasaulx, *Jahrbuch f. Mineralogie*, 1874, 142). This mineral has hitherto been found mostly associated with trachytic rocks or breccias in such a manner as to indicate its formation by volcanic exhalations. The oldest known alunites, namely, those of Piombino and La Tolfa, near Civita Vecchia, are very intimately mixed with trachitic tufas and pumice-conglomerates, into which they directly pass. Similar is the mode of occurrence of the alunites of Aegina, of Bereghszász, Tokay, and Musaj in Hungary, and of Mont Dore in Auvergne. In all these cases the transformation of the trachytes has been produced by exhalations of sulphydric acid mixed with sulphurous or sulphuric acid. In the Hungarian alunites, according to v. Richthofen, the process has been commenced by exhalations of hydrofluoric acid, and the silicofluorides thereby produced have been converted into sulphates by aqueous vapours containing sulphuric acid. Somewhat different relations must have existed when the original rock was not trachyte, but impure sandstone, as appears to have been the case with the alum-stone of Kawa Tjiwidai in Java, and with that of Musaj in Hungary. In these cases the transformation has probably been effected by sulphurous acid during a period of volcanic activity.

Another mode of formation is exhibited by an alunite from a recently opened deposit near the village of Breuil, west of Issoire in Auvergne. This alunite is white, varied here and there with pale red, earthy, loose, and friable throughout, and adheres very strongly to the tongue. Under the microscope it exhibits the appearance of small roundish granules without crystalline structure. Quartz in granules and splinters is sparingly disseminated through the mass; the substance gives off water when heated in a tube, and emits an odour of sulphurous acid even when very slightly heated. When ignited with cobalt-solution it acquires a fine blue colour. Sp. gr. = 2.601.

The composition of this alunite is shown in analysis I, by Truchot. II shows the composition of the pure alunite after deduction of the silica, which must be regarded as an impurity. III and IV are analyses of alunite from Pic de Sancy in Auvergne. III is by Cordier, after deduction of 28.4 per cent. silica and 1.44 ferric oxide. IV is by Gautier-Lacroze (*Jahrbuch*, 1864, 723), after deduction of 36.2 per cent. silica, ferric oxide, and sulphur:—

	I.	II.	III.	IV.
SO ²	37.6	40.9	39.1	36.4
Al ² O ³	38.3	41.8	46.5	39.5
K ² O	7.2	7.9	8.5	8.8
Fe ² O	trace	—	—	—
SiO ²	8.2	—	—	—
H ² O	8.5	9.2	5.9	15.4
	<hr/> 99.8	<hr/> 99.8	<hr/> 100.0	<hr/> 100.1

The last two analyses give an amount of alumina larger than is required, according to the quantity of sulphuric acid, to form potassio-aluminic sulphate. The higher amount of water in IV points to the presence of aluminium hydrate, therefore probably to an admixture of gibbsite, whilst Cordier's analysis (III) agrees nearly with Mitscherlich's formula of alunite, viz.:—



the proportion of alumina, however, being somewhat less than that required by this formula. The alunite of Breuil, on the other hand, contains sulphuric acid, alumina, and potash almost exactly in the proportions required to form aluminium monosulphate and potassium sulphate, so that this alunite may be regarded with tolerable certainty as a simple hydrate of these two salts, represented by the formula:



It is therefore extremely rich in aluminium monosulphate, a peculiarity probably due to its mode of formation.

The Breuil alunite appears as the coating of a bed of red ferruginous clay, forming part of the trachytic tufas and basaltic and pumiceiferous conglomerates extending in the form of hills and table-lands over the whole district west of Issoire. This mode of occurrence distinguishes it from that of the other alunites above mentioned. The manner in which it encloses the ferruginous clay indicates a regularity of transformation which can scarcely be attributed to exhalations attacking the clay from all sides and without order, but rather points to an action originating within the mass of the clay itself. The formation of the alunite may in fact be attributed to the decomposition of iron pyrites, or more probably of marcasite, in the clay, brought about by the action of rain-water. The marcasite, by oxidation, would yield ferrous sul-

phate and free sulphuric acid, and the sulphuric acid penetrating outwards would convert the exterior portion of the clay bed into alunite. This transformation may in fact be imitated experimentally, by laying marcasite on a mud of clay-slate containing potash, and leaving it exposed to moisture. After some time a solution is obtained, which by gradual evaporation yields a mixture of ferrous sulphate and alum. Then, as the decomposition advances, the ferrous sulphate is robbed of its sulphuric acid, which goes to complete the formation of the alunite, and as insoluble residue there remains nothing but ferric oxide, which gives the red colour to the nucleus of clay. Beds of alunite, containing red hæmatite and gypsum, together with iron-glance, like those of the Musaj mountains, have probably been formed in the same way.

There are, then, two modes of formation of alunite, first by the action of sulphuric acid exhalations on rocks containing alumina, ferric oxide, and potash, the products in this case being alunite, pyrites and sulphur; secondly, from pyrites or marcasite, the final products of which are alunite, iron-glance, and red hæmatite. Both these modes of formation are exhibited in the district of Mont Dore, the former at the Ravin de la Craie, the latter at Breuil.

AMARINE, $C^2H^{10}N^2$. From the difference of action of ethyl iodide on the isomeric compounds, hydrobenzamide and amarine, Borodin inferred that in hydrobenzamide, $(C^6H^5.CH)^2N^2$, the whole of the hydrogen is in immediate combination with carbon, whereas in amarine, $N \left\{ \begin{smallmatrix} N(C^6H^5)H \\ ||^2 \end{smallmatrix} \right.$, two of the hydrogen-atoms belong to the ammonia residue (iii. 184). On this view, the conversion of hydrobenzamide by boiling into amarine is exactly analogous to that of tertiary amines (dimethylaniline, for example) into secondary and primary amines observed by Hofmann (*2nd Suppl.* 57). In both cases hydrogen-atoms are transferred from the carbon to the nitrogen, and carbon-atoms are linked together, producing, on the one hand, ammonia-residues, and on the other carbon-groups of higher order. In the case of hydrobenzamide, however, this transformation takes place much more easily than with the aniline derivatives (Borodin, *Deut. Chem. Ges. Ber.* vi. 1253).

Nitrosamarine, $C^2H^{10}(NO)N^2$ (Borodin, *Deut. Chem. Ges. Ber.* viii. 933).—This compound is best prepared by adding a concentrated, hot, alcoholic solution of an amarine salt (hydrochloride, nitrate, or acetate), acidified with acetic acid, to a very concentrated, hot, aqueous solution of an alkaline nitrite, also acidified with acetic acid. On stirring the mixture, a lively reaction takes place, ethyl nitrite and nitrogen being evolved, and the yellow liquid becoming filled with small, heavy, brilliant laminae, which refract light strongly, and have a rhombic or triangular form. The deposition of crystals continues for some time after the liquid is cold.

The formation of nitrosamarine takes place also, though less quickly, in dilute alcoholic solutions, and may be used as a test for the presence of amarine salts. In aqueous solutions it takes place only when both liquids are concentrated.

The direct action of nitrous acid on amarine and its salts gives rise, not to nitrosamarine, but to a peculiar complex body containing nitrogen and oxygen.

Nitrosamarine is insoluble in water and is not wetted thereby. It dissolves in alcohol, ether, amylic-alcohol, carbon bisulphide, benzene, and hydrocarbons. It is not volatile: at 149° – 150° it cakes together, turns brown, and is perfectly decomposed, with abundant evolution of nitrogen and nitric oxide, and formation of a large quantity of lophine, and a smaller quantity of a liquid which has the smell of oil of bitter almonds. Nitrosamarine is also attacked by an alcoholic solution of caustic potash, with formation of lophine, ammonia, and a liquid smelling of bitter almonds, but it is scarcely affected by an alcoholic solution of ammonia, even at a boiling heat. When it is gently warmed with sulphuric, hydrochloric, or nitric acid in presence of alcohol, heat is liberated and the substance dissolves, with abundant evolution of nitrogen, and formation of ethyl nitrite and amarine, the salt of which, with the acid used, remains in the solution. When mixed with acids in presence of water, it is not so readily attacked in the cold, but is decomposed on heating, with formation of amarine and evolution of nitric oxide and nitrogen. It behaves similarly towards acetic acid. This behaviour towards acids places nitrosamarine among the nitroso-derivatives of known imide bases (diethylamine, piperidine, conine). It gives, also, the characteristic colour reactions of the nitroso-compounds with phenol.

AMBER. On the identity of the so-called 'unripe amber,' from the coast of the Baltic, with Krantzite, see RESINS, FOSSIL (*2nd Suppl.* 1039).

AMESITE. This name was given by Shepard to a mineral found on some diaspore at Chester (Mass.) It occurs in small crystalline masses, formed of super-

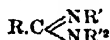
posed layers,* of hexagonal appearance, with easy cleavage parallel to the base, accompanied by scattered needles of rutile. Translucent in thin plates. A thin plate exhibits a positive optic axis with the polarising microscope. Lustre pearly. Colour pale apple-green. Hardness 2.5 to 3. Density 2.71. Before the blowpipe it becomes blackish and is almost infusible. Composition:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	H ₂ O.
22.40	32.30	15.80	19.90	10.90

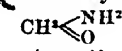
(Pisani, *Compt. rend.* lxxxiii. 166).*

AMETHYST. On Twin-formations of Amethyst, see *Jahrbuch f. Mineralogie*, 1874, 428; 1875, 190.

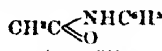
AMIDES (Wallach, *Deut. Chem. Ges. Ber.* viii. 1575). Phosphorus pentachloride acting on acid amides, R.CONR² (where R or R' represents hydrogen or a hydrocarbon radicle), produces bodies of the formula R.CCINR'; and those when acted upon by an amine yield bases, called amidines or amimides, and represented by the formula,



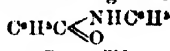
Thus to every acid amide there is a corresponding amidine which may be regarded as derived from it by the substitution of NR' for O. The following are examples:—



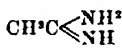
Acetamide.



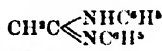
Acetanilide.



Benzanilide.



Acetdiamine.



Ethenyldiphenylamidide.



Benzenyldiphenylamidide.

Similarly with the amides of bibasic acids:—



Carbamide.



Guanidine.

Amidines are formed also from thiamides by the exchange of S for NR'; guanidine, for instance, being formed by the action of amines on thiocarbamide.

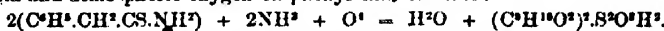
The amidines, as a class, are remarkable for the facility with which they react with water to form the amides from which they are derived. Thus ethenyldiphenylamidide is resolved by prolonged boiling with weak spirit, or even by oft-repeated crystallisation therefrom, into acetanilide and aniline:—



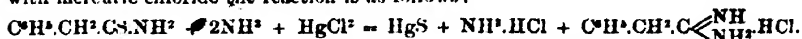
Similarly, guanidine yields carbamide and ammonia, and acediamine breaks up with extreme facility into acetamide and ammonia.

Phenyl-acetamidide or Phenylacediamine, $C^6H^5N^2 = C^6H^5.CH^3.C \begin{matrix} \nwarrow NH \\ \nearrow NH^2 \end{matrix}$

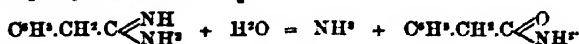
(Bernthsen, *Deut. Chem. Ges. Ber.* viii. 1319; ix. 429). This base, the acediamine of the α -toluic series, is formed: 1. As a thiosulphate, by the simultaneous action of ammonia and atmospheric oxygen on phenyl-thioacetamide:



2. By the action of desulphurising agents on phenyl-thioacetamide and ammonia; with mercuric chloride the reaction is as follows:—



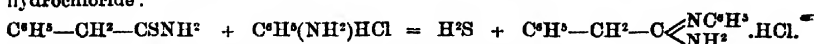
The base, separated from its salts by heating with potash, forms oily drops which solidify on standing to a mass of platy crystals. It dissolves easily in alcohol, ether, warm water, and dilute potash; melts at 83°–89°; cannot be sublimed without decomposition; and in contact with potash, evolves a small quantity of ammonia. It absorbs carbonic acid from the air. Alcohol and water decompose it, with formation of ammonia and phenylacetamide:



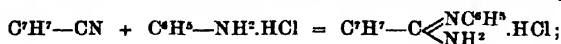
The acid sulphate of phenylacetamidide forms large tabular crystals, easily soluble in water and in alcohol. The thiosulphate crystallises from alcohol in white needles, and from water in thick prisms which are frequently hollow; it is almost insoluble

in ether, slightly soluble in alcohol and cold water, easily in hot water. • The acetate, $C^6H^{10}N^2.C^2H^4O^2$, obtained by decomposing the thiosulphate with lead acetate, crystallises from alcohol in stellate groups of slender needles, easily soluble in water and in alcohol, nearly insoluble in ether, melting at 192° – 193° . The neutral oxalate forms white prisms or needles, soluble in water and in alcohol. The acid oxalate, which is less soluble, crystallises in matted needles. The nitrate and hydrochloride are crystallisable.

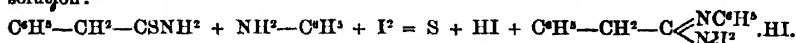
Phenylacetomonophenylamidide, $C^6H^4N^2 \rightleftharpoons C^6H^5.CH^2.C \begin{smallmatrix} \text{NC}^6H^5 \\ \text{NH}^2 \end{smallmatrix}$, is formed, with evolution of hydrogen sulphide, when phenyl-thiacetamide is heated with aniline hydrochloride:



The same base is formed by the reaction of benzyl cyanide and aniline hydrochloride:



also by the action of iodine on a mixture of aniline and phenyl-thiacetamide in alcoholic solution:



Phenylacetomonophenylamidide forms small white needles or laminae, melting at about 128° , and subliming in long needles. It dissolves sparingly in water and very freely in alcohol and ether. It is a mon-acid base, forming salts which, with the exception of the oxalate, are not crystallisable.

Phenylacetomonotolylamidide, $C^6H^5-CH^2-C \begin{smallmatrix} \text{NC}^6H^7 \\ \text{NH}^2 \end{smallmatrix}$, a base analogous to the foregoing, is obtained by similar reactions, toluidine hydrochloride being employed instead of the aniline salt. It crystallises in thick prisms, which dissolve in water, alcohol, and ether, melt at 118° – 119° , and sublime at a higher temperature. Its salts are more easily crystallisable than those of the phenyl base.

Benzonyl-monophenylamidide, $C^{10}H^{12}N^2 = C^6H^5-C \begin{smallmatrix} \text{N.C}^6H^5 \\ \text{NH}^2 \end{smallmatrix}$, formed by the action of aniline hydrochloride on thiobenzamide, $C^6H^5.GS.NH^2$, or benzonitril (phenyl cyanide) is a white substance, easily soluble in water, and forming salts which are mostly uncrystallisable.

Benzonyl-diphenylamidide, $C^{10}H^{10}N^2 = C^6H^5-C \begin{smallmatrix} \text{N.C}^6H^5 \\ \text{NHC}^6H^5 \end{smallmatrix}$, formed by the action of aniline on the preceding, is nearly insoluble in water. It is identical with the product which Gerhardt obtained by the action of PCl^5 on benzanilide.

Benzonyl-monotolylamidide, $C^6H^5-C \begin{smallmatrix} \text{NC}^6H^7 \\ \text{NH}^2 \end{smallmatrix}$, formed by the action of benzonitril on toluidine hydrochloride, crystallises in transparent tables melting at 99° – 99.5° . The oxalate and nitrate crystallise in needles.

Benzonyl-ditolylamidide, $C^6H^5-C \begin{smallmatrix} \text{NC}^6H^7 \\ \text{NHC}^6H^7 \end{smallmatrix}$, formed, together with the preceding base, crystallises in thick yellowish prisms less freely soluble than the monotolyl base. It melts at 131° – 132° , and sublimes at a higher temperature.

AMMELIDE. Liebig represented this body by the formula $C^6H^5N^2O^2 = (C^6H^5)(NH^2)(OH)^2$; Gerhardt regarded it as $C^6H^5N^2O^2 = (C^6H^5)(NH^2)(OH)^2$ (ii. 287). The first of these formulæ requires 49.41 per cent., the second 48.75 per cent. nitrogen. Gabriel (*Deut. Chem. Ges. Ber.* viii. 1166) finds that ammelide, prepared by calcination of ammeline nitrate, contains 50.71–51.59 per cent. nitrogen; that prepared by the action of nitric acid on melam (Knapp's process, see *Gmelin's Handbook*, ix. 476) contains 51.02–51.44 per cent.; and the product obtained by the action of sulphuric acid on pure melam contains a still larger quantity of nitrogen.

On the other hand, a white chalky product obtained by dissolving crude melam in hot strong sulphuric acid, precipitating with alcohol, and washing the precipitate thoroughly with boiling water, exhibited a constant composition agreeing exactly with that of Gerhardt's ammelide, and of Liebig & Wöhler's melanurenic acid, obtained by calcining urea. This compound combines readily with nitric and hydrochloric acids, as previously pointed out by Volhard (*Deut. Chem. Ges. Ber.* vii. 92). The nitrate, $C^6H^5N^2O^2.HNO^3$, crystallises in shining scales; the hydrochloride, $C^6H^5N^2O^2.HCl$, in microscopic needles.

AMMONIA. *Formation.*—Ammonia may be produced synthetically by the action of induced electricity on a mixture of nitrogen and hydrogen in the proper

proportion. The quantity thus formed is small, but sufficient to give a decided red-brown precipitate with Nessler's reagent.

Absorption.—1. By Ammonium Nitrate. See NITRATES (2nd Suppl. 859).

2. By Saline Solutions.—F. M. Raoult (*Compt. rend.* lxxvii. 1078; *Ann. Ch. Phys.* [5], i. 262) has studied the absorption of ammonia gas by solutions of salts which it does not decompose or precipitate. Experiments on the absorption of ammonia by water confirmed the results of Roscoe & Dittmar (*Gases*, ii. 708). For solution of potassium hydrate, the coefficient of absorption is less than that for pure water, in proportion as the solution is more concentrated. At 16° and 760 mm. barometric pressure, 100 c.c. of water absorb 60 grams of ammonia, whereas 100 c.c. of aqueous potash containing 24.25 per cent. KHO absorb only 30 grams, and 100 c.c. of a saturated potash-solution absorb only 1 gram of ammonia. Soda-solutions have the same absorption-coefficient as potash-solutions of like concentration. Solutions of sodium nitrate and of ammonium nitrate absorb exactly as much ammonia as water does, although dry sodium nitrate absorbs no ammonia, and dry ammonium nitrate absorbs a considerable quantity. A solution of potassium nitrate absorbs more ammonia than water absorbs, but the residue obtained by spontaneous evaporation is free from ammonia; the absorption under varying pressure conforms almost exactly to Dalton's law, and develops an amount of heat equal to that evolved in the absorption of ammonia by water, so that we cannot suppose that the ammonia exerts any decomposing action on the salt.

With saline solutions whose boiling point does not exceed 110° the following law holds good:—*The difference between the coefficient of absorption of ammonia in water, and in solutions of the same salt of different degrees of concentration, is proportional to the weight of salt contained in a constant volume measured before the absorption of the gas.*

To solutions of caustic potash or soda this law is applicable only when they contain less than 1 mol. of anhydrous base to 16 mols. of water. More concentrated alkaline solutions dissolve more ammonia than the law indicates. Such a solution of potash, for example, dissolves 16 times its volume of ammonia. Even the solid hydrates, with the exception of the mono-hydrates, KHO and NaHO, absorb a little of the gas. The general law above named furnishes an explanation of the well-known fact that a concentrated solution of ammonia evolves a portion of its gas when potash is added to it. The potash but slightly increases the bulk of the liquid, and at the same time it forms a solution less capable than water of absorbing ammonia. Solutions of ammonium chloride dissolve a little less ammonia than water absorbs.

3. By Plants. See NUTRITION, VEGETABLE.

On the Exchange of Ammonia between Air, Water, and Soil, see Schlossing (*Compt. rend.* lxxxi. 81, 1252, lxxxii. 747, 846, 969; *Chem. Soc. Jour.* 1876, i. 95, 518; ii. 44, 172).

Detection.—According to G. C. Wittstein (*Arch. Pharm.* [3], iii. 327), a solution of mercuric chloride (as originally pointed out by Eilbrodt), is a more delicate test for ammonia than Nessler's reagent. In support of this view the following experiment is adduced:—Into one of two beakers, each containing 100 c.c. of water, were introduced 1 drop of ammonium chloride solution, 1 drop of potash solution, and 1 drop of mercuric chloride solution, and into the other 1 drop of ammonium chloride solution, and 5 drops of Nessler's reagent. In the first beaker a distinct white opalescence was produced; in the second neither coloration nor turbidity was perceptible, even after the addition of more Nessler's reagent. Compare Guyot (2nd Suppl. 59).

According to J. Moddermann (*Chem. Centr.* 1873. 677), the presence of ammonia in distilled water may be detected by means of cupric sulphate. A certain quantity of distilled water dissolves this salt without turbidity; but on adding more distilled water, there occurs, at a particular degree of dilution, a greenish turbidity, followed by the gradual deposition of a green precipitate consisting of basic cupric sulphate. The formation of this compound is due to ammonia, which is invariably present in ordinary distilled water. To the same cause is due the turbidity produced in a neutral solution of ferric chloride by a large quantity of distilled water.

Estimation.—In the estimation of ammonia by distilling ammonium salts with caustic alkali, an error may arise from the presence of thiocyanates, which also liberate ammonia under these circumstances. This error may, however, be completely avoided by using lime or baryta, preferably the latter, in place of potash or soda (A. Eilmann, *Chem. News*, xxxi. 15).

On the Estimation of Ammonia by Nessler's Reagent, see S. Harvey (*Chem. News*, xxvii. 262; *Chem. Soc. Jour.* [2], xi. 1161).

On the Estimation of Ammonia in the Air, see Schlossing (*Compt. rend.* lxxx. 265; *Chem. Soc. Jour.* [2], xiii. 663).

Estimation in Coal Gas.—Houzeau (*Compt. rend.* lxxvi. 52) passes the gas through 5 c.c. of dilute sulphuric acid, containing 0.30825 grm. SO_4H^2 , until the liquid, previously tinged with litmus, assumes a blue colour. The current of gas is then arrested, and the volume which has passed is noted. This volume of gas contains 0.10625 grms. NH_3 .

Estimation of Ammonia, Organic Nitrogen and Nitric Acid in Water, Earth, &c.—Piuggari (*Compt. rend.* lxxvii. 481) employs for this purpose a method, called *Ammonio-nitrometry*, which consists in first determining the free ammonia either with Nessler's reagent, or by adding one or two drops of phenol to 5.6 c.c. of sodium hypochlorite, and comparing the violet-blue colour produced with a normal solution. The nitrogen existing as organic matter is oxidised to nitrous and nitric acids by heating with a mixture of silver chloride and caustic potash to 50° – 60° for several hours, then reduced to ammonia with potash and aluminium-foil, and estimated as before. By alternate reduction and oxidation, nitrogen in the three forms of combination may be estimated in one portion.

Anhydrous Liquid Ammonia.—G. Gore (*Proc. Roy. Soc.* xx. 441) has examined the solvent action of liquid ammonia on various substances, by means of an apparatus similar to that which he formerly employed for the examination of liquid cyanogen (*2nd Suppl.* 416), the tubes being charged with calcium chloride previously saturated with ammonia gas.

The only elementary substances soluble in the liquefied ammonia are the alkali-metals proper, iodine (bromine was not tried), sulphur, and phosphorus. The more generally soluble inorganic salts are nitrates, chlorides, bromides, and iodides; whilst oxides, fluorides, carbonates, sulphides, and sulphates are very generally insoluble. Many saline substances, especially certain chlorides, bromides, iodides, and sulphates, absorb ammonia freely, and swell greatly, but do not dissolve.

Various compounds of carbon were submitted to the action of the solution of potassium in the liquefied vapour; the free potassium disappeared, but no elementary carbon was liberated.

AMMONIA-SODA PROCESS. See SODA MANUFACTURE.

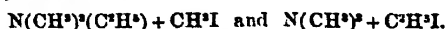
AMMONIO-NITROMETRY. See above.

AMMONIUM AMALGAM. Routledge (*Chem. News*, xxvi. 210) has determined the volume-relation of the ammonia and hydrogen evolved from this substance, by first measuring the total volume of gas, then absorbing the ammonia by water, and finally reading off the residual volume. In this way it is found that the volumes of ammonia-gas and hydrogen evolved are very nearly in the ratio 2 : 1, leading to the inference that the ammonium and hydrogen in the amalgam are chemically combined.

When the amalgam is subjected to varying pressure, its volume varies nearly in the inverse ratio of the pressure, whence it appears that the increased volume of the amalgam is due to free gases enclosed within its mass. A compound of ammonium and mercury is probably formed in the first instance, but this compound immediately begins to decompose, the ammonia and hydrogen evolved becoming entangled in the mercury, and causing it to swell up.—Compare *1st Suppl.* p. 104.

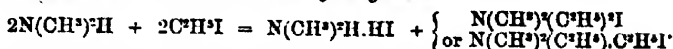
AMMONIUM SALTS. The question as to whether these salts should be regarded as derivatives of quinquivalent nitrogen, or as molecular compounds containing trivalent nitrogen—sal-ammoniac, for example—either as $\frac{\text{H}^1}{\text{Cl}}\text{N}$ or as $\text{H}^1\text{N} + \text{HCl}$, being still undecided, Meyer and Lecco (*Doit. Chem. Ges. Ber.* vii. 1748; viii. 233, 938) have endeavoured to solve it by the examination of certain salts of compound ammoniums.

If trimethylamine be combined with ethyl iodide and dimethyl-ethylamine with methyl iodide, the resulting ammonium iodides must be identical, if the ammonium salts have the constitution indicated by the first of the above formulæ, since they will both in fact consist of dimethyl-diethyl-ammonium iodide, $\left(\frac{\text{CH}_3}{\text{C}^2\text{H}_5}\right)_2\text{N}^1\text{I}$. But if sal-ammoniac and its analogues are molecular aggregates, the compounds in question must be different, the one containing a molecule of methyl iodide, the other a molecule of ethyl iodide, thus:



To compare these two compounds it was necessary in the first place to prepare dimethyl-ethylamine, and for this purpose dimethylamine was subjected to the action of ethyl iodide. This reaction, however, yielded, not the hydriodide of dimethyl-ethylamine, as might have been expected from the analogous reaction by which triethyl-

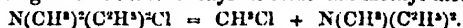
amine is obtained (ii. 559), but hydriodide of dimethylamine and iodide of dimethyl-diethyl-ammonium, or ethiodide of dimethyl-ethylamine:



The resulting liquid treated with caustic potash deposited the second compound, and on adding hydrochloric acid to this precipitate, to neutralise the adhering potash, and mixing it with recently precipitated silver chloride, silver iodide was formed, together with ethylchloride of dimethyl-ethylamine, $\text{N}(\text{CH}_3)_2(\text{C}^2\text{H}_5)_2.\text{C}^2\text{H}_5\text{Cl}$, which was easily separated from the potassium chloride by solution in cold alcohol and evaporation.

In like manner, by heating diethylamine with methyl iodide, and proceeding exactly as above described, the methyl-chloride of diethyl-methylamine, $\text{N}(\text{CH}_3)(\text{C}^2\text{H}_5)_2.\text{CH}_3\text{Cl}$, was obtained.

The two chlorides thus produced resemble one another exactly, in every respect. Treated with moist silver oxide, they yield a base, the sulphate and nitrate of which are identical in properties from whichever of the two chlorides they may be prepared. The platinumchlorides, aurochlorides, and picrates derived from the two are likewise identical, and finally the two chlorides undergo exactly the same decomposition by dry distillation, being resolved into methyl chloride and methyl-diethylamine:



It must, therefore, be concluded that these chlorides are not really different, but that, whether we start from dimethylamine and ethyl iodide, or from diethylamine and methyl iodide, the salt obtained is the same, viz., the iodide of dimethyl-diethyl-ammonium, $(\text{CH}_3)_2(\text{C}^2\text{H}_5)_2\text{N.I}$, the nitrogen contained in it being quinquivalent, and the compound itself not molecular but atomic; and hence it may be inferred, as in the highest degree probable, that a similar constitution belongs to all the ammonium salts, including sal-ammoniac. These conclusions have been criticised by W. Losson (*Liebig's Annalen*, clxxi. 364; *Chem. Soc. Jour.* 1876, ii. 629); also by Ladenburg. —See NITROGEN.

Decomposition of Ammonium Salts in Aqueous Solution.—When solutions of different ammonium salts are boiled, a definite quantity of ammonia is lost, the amount depending, not only on the bulk and concentration of the solution and quantity of water evaporated, but also on the nature of the salt. It is, therefore, possible to infer, from the amount of ammonia liberated under defined conditions, the nature or the quantity of the ammoniacal salts present. This observation may be applied to decide the question as to whether two salts which cannot form an insoluble compound do nevertheless partially decompose each other in a solution or not. Experiment shows that such solutions contain at 100° four salts, the relative quantities of which depend upon the proportions in which the original salts were brought together.

The effect produced by the presence of other salts on the dissociation of ammonium salts may be determined by comparing the amount of ammonia which escapes from the simple solution with that liberated when another salt of the same acid is also present. At the boiling point the differences are very small, but they seem to show that more ammonia is volatilised when the ammonium salts are boiled alone. At ordinary temperatures, on the other hand, more ammonia evaporates in a given time from the mixed solution than from the simple one, and its proportion to the quantity of water simultaneously evaporated is also always higher (Dibbits, *Pogg. Ann. Ergänzungsband*, vii. 462).

AMYL ALCOHOLS. 1. *Isoprimary.*—The statements of different observers respecting the optical properties of the amyl alcohols obtained from fusel oil are somewhat discordant. It is commonly stated that, by Pasteur's method, founded on the fractional crystallisation of the barium salts of the corresponding amylsulphuric acids (i. 203), or by Chappman a. Smith's method of saturation with caustic alkali or calcic chloride, and subsequent distillation (*1st Suppl.* 107), two amyl alcohols are obtained, one optically laevogyrate, the other inactive to polarised light. N. Ley, however (*Deut. Chem. Ges. Ber.* vi. 1862), finds that, by repeated application of Pasteur's method, two laevogyrate amyl alcohols may be obtained of unequal rotatory power. One of these alcohols exhibited a laevo-rotatory power much greater than that of the active amyl alcohol obtained by previous observers, producing a rotation of 46° in a column 50 centimeters long, and equivalent to that of a solution of 4.7 pts. of sugar in 100 of water, whereas the alcohol obtained by Erlenmeyer a. Hell (*Ann. Ch. Pharm.* clx. 257) exhibited in a column of the same length a rotation of only 23°, equivalent to that produced by a 2.4 per cent. solution of sugar, and that obtained by Le Bel (*in/ra*) had nearly the same rotatory power.

The less active alcohol obtained by Ley had a rotatory power equivalent to that

of a 1.04 per cent. sugar-solution, and somewhat less than that of the amyl alcohol studied by Pierre a. Puchot (2nd Suppl. 62).

The following table exhibits a comparison of the rotatory powers, boiling points, and specific gravities of the active amyl alcohols according to different observers:—

Observer.	Apparatus unknown.	Sollet's apparatus. Tube 200 mm.	Ventzke-Sollet apparatus. Tube 500 mm.	Corresponding with sugar dissolved in 100 parts of water.	Boiling-point.	Specific gravity.
Pasteur	-20°	—	—	—	127°—128°	—
Pedler	-17°	—	—	—	128°	—
Erlenmeyer and Hell	—	—	-23	2.4	125°—130° greater part at 127.5°	.812 at 19°
Pierre and Puchot	—	-8	—	1.4	130°	.825 at 0°
Ley (more active)	—	—	-46	4.7	128°	.808 at 15°
" (less active)	—	—	-10	1.04	131°	.816 at 15°

From this comparison, Ley infers that the two alcohols have not yet been obtained quite pure.

According to Popoff (*Deut. Chem. Ges. Ber.* vi. 560) commercial amyl alcohol, if directly subjected to fractional distillation, yields in the first portion of the distillate an amyl alcohol of stronger rotatory power than the original liquid; but, if previously digested with caustic alkali or calcium chloride, according to Chapman's Smith's method, it no longer yields by fractional distillation a more active alcohol.

J. A. Le Bel (*Compt. rend.* lxxvii. 1021) separates optically active amyl alcohol from the mixed fermentation alcohols, by means of hydrochloric acid, whereby the inactive (or less active) alcohol is converted into amyl chloride before the more active alcohol. Gaseous hydrogen chloride is passed into crude amyl alcohol contained in a flask fitted with a reflux apparatus, and the portion boiling below 120° is distilled off from time to time. The distillate is freed from the greater part of the hydrochloric acid by a second distillation, then neutralised with potassium carbonate and dried; the alcohol and the chloride are separated by fractional distillation; and the alcohol is again treated with hydrogen chloride. By repeating this series of processes till nine-tenths of the original mixture of alcohols is converted into chloride, an amyl alcohol is obtained which boils at 127°, and in a column 50 centimeters long deflects the plane of polarisation 22.5°. The alcohol prepared as above still, however, contained a small quantity of the inactive alcohol.

Inactive amyl alcohol and its ethers have been examined by Balbiano (*Gazz. chim. ital.* vi. 220). In preparing it by Pasteur's method, the fractional crystallisation of the mixed barium amyl sulphates had to be performed 18 or 20 times before the salt from the inactive alcohol presented the constant solubility at 10° of 9.7 parts to 100 of water. Fermentation butyl alcohol was also converted into valeric acid and then into amyl alcohol in the ordinary way. This synthetically formed alcohol yielded a barium amylsulphate having precisely the same degree of solubility as that of the salt obtained from the inactive amyl alcohol, so that there can be but little doubt that the inactive alcohol is strictly homologous with fermentation butyl alcohol and has the constitution represented by the formula $\text{CH}^3\cdot\text{CH}(\text{CH}^3)\cdot\text{CH}^2\cdot\text{CH}^2(\text{OH})$.

The pure inactive amyl alcohol is obtained from the barium salt by digesting it for several hours with a slight excess of dilute sulphuric acid, and then distilling, when the whole of the alcohol passes over with the first portion of the distillate. When dried it is a colourless liquid, which has no perceptible action on polarised light in a column 40 centimeters long. It boils at 131.4° with the thermometer in the vapour, and under a pressure of 747 mm. (reduced to 0°). Its density at 0° is 0.8238. It dissolves in about 50 volumes of water at 14°, and the solution becomes milky when heated to 50°. Neither the pure inactive alcohol nor the crude mixture of amyl alcohols is altered when heated to 250° either in the dry state or in presence of water.

The amyl chloride prepared by heating a saturated solution of hydrochloric acid in the inactive alcohol at 105° is an optically inactive colourless liquid, boiling at 98.9°

under a pressure of 733.8. Its density at 0° is 0.8928. *Amyl bromide* prepared in a manner precisely similar to the chloride boils at 120.4° under a pressure of 745.2. Its density at 0° is 1.2358. *Amyl acetate* is a colourless, optically inactive liquid, prepared by distilling a mixture of acid amyl sulphate and dry sodium acetate. It boils at 138.6° under a pressure of 743.5, and its density at 0° is 0.8838. *Amyl valerate*, obtained together with some valeric aldehyde and traces of valeric acid, by Pierre and Puchot's method of oxidising the alcohol at a low temperature by means of chromic acid mixture, is optically inactive. It boils at 190.3° under a pressure of 748, and has a specific gravity of 0.870 at 0°. When decomposed by an alcoholic solution of potassium hydrate, it yields potassium valerate, from which the inactive valeric acid may be obtained by distilling it with dilute sulphuric acid. When dry it boils constantly at 174.1°, under a pressure of 723.5°.

Dextrogyrate Amyl Alcohol (?)—According to G. H. Beignes Bakhoven (*Pogg. Ann. Ergänzbd.* vi. 325) a dextrogyrate alcohol is obtained by repeated distillation of commercial amyl alcohol with solid sodium hydrate. The rotatory power of the original levogyrate liquid then steadily diminishes; the alcohol after a while becomes dextrogyrate; and after ten or twelve distillations an alcohol is obtained which boils at 133°–134°, and has a constant dextro-rotatory power, producing a deviation of ten degrees in a column 50 centimeters long, or four degrees in a column of 20 centimeters.

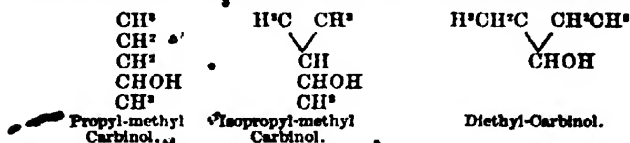
These statements, however, have not been confirmed by other observers. Le Bel (*Compt. rend.* lxxxii. 562), in repeating Bakhoven's experiments, was unable to discover a trace of the dextrogyrate alcohol, and considers it probable that the body in question was really a mixture of the inactive alcohol with amyl oxide, which is dextrogyrate. Balbiano also (*Gazz. chim. ital.* vi. 402) found that inactive amyl alcohol remained inactive after thirty-two distillations from sodium hydrate; and that the commercial alcohol was rendered inactive by twenty-three distillations; whereas no dextro-rotatory alcohol was obtained even after forty-three distillations. By these repeated distillations a small quantity of amyl oxide was formed, and a corresponding quantity of water eliminated.

Detection of Amyl Alcohol in presence of Ethyl Alcohol.—About 5 c. c. of the alcohol to be examined is diluted with 6 or 7 vols. of water, and 16 to 20 drops of chloroform are added, after which the mixture is shaken and then left at rest. The amyl alcohol will then be carried down by the chloroform, and left behind after the spontaneous evaporation of the latter (Bettelli, *Gazz. chim. ital.* iv. 566).

Action of the Copper-zinc Couple on Amyl Iodide.—Ordinary amyl iodide is not acted on by the copper-zinc couple at 100°, and if the temperature be raised to its boiling point, secondary products are formed. At 145°, however, zinc-amyl iodide, $\text{Zn}\left\{\begin{smallmatrix} \text{C}^5\text{H}^{11} \\ \text{I} \end{smallmatrix}\right.$, is obtained as a crystalline solid, together with amyl hydride (pentane), amylene and diamyl. On distilling the product, zinc-amyl, $\text{Zn}(\text{C}^5\text{H}^{11})_2$, is obtained, amounting to 20–30 per cent. of the quantity which should be formed by the decomposition of the compound $\text{Zn}(\text{C}^5\text{H}^{11})\text{I}$, together with hydrocarbons, from which it may be separated by fractional distillation. By distillation in a vacuum, the crystalline compound yields about 40 per cent. of the theoretical quantity of zinc-amyl.

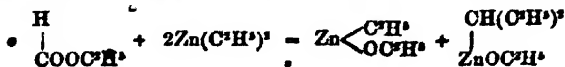
In presence of water or alcohol, the action of the couple on amyl iodide is exactly analogous to that which it exerts on ethyl iodide (2nd Suppl. 480), yielding pentane, C^5H^{12} , together with iodhydrate or iodethylate of zinc (Gladstone & Tribe, *Chem. Soc. Jour.* [2], xi. 678).

Secondary Amyl Alcohol. *Diethyl-carbinol* (Wagner & Saytzeff, *Annalen der Chemie*, clxxv. 361).—Of the three possible secondary amyl alcohols, viz.—

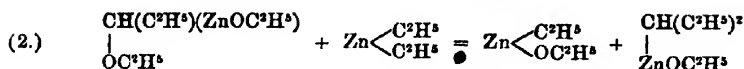
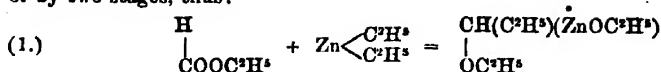


The first two only have hitherto been known (1st Suppl. 111). The third is obtained by heating ethyl formate with zinc-ethyl, and decomposing the product with water.

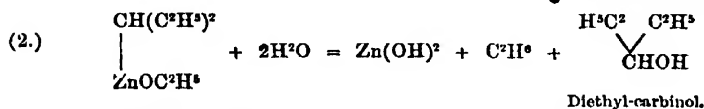
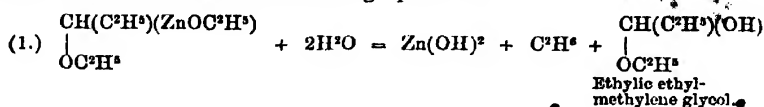
The reaction between ethyl formate and zinc-ethyl may be supposed to take place either in one stage, as represented by the equation:



or by two stages, thus:—



The second view is the more probable of the two, inasmuch as the reaction does not exhibit the same phenomena throughout, but begins with the conversion of the reacting liquids into a syrupy mass, which gradually becomes solid and crystalline. This solidification may be regarded as the second stage and end of the reaction; for it is found that the more completely the product is solidified, the larger is the quantity of diethyl-carbinol obtained on treating it with water, whereas the syrupy mass, which is the first product, yields no diethyl-carbinol when treated with water. This is in accordance with the following equations:



The intermediate product, ethylic ethyl-methylene glycol, has not yet been isolated.

Preparation of Diethyl-carbinol.—Instead of using ready-formed zinc-ethyl, it is better to evolve it in the nascent state by the action of zinc on ethyl iodide. A mixture of 1 mol. ethyl formate and 4 mols. ethyl iodide is heated in a flask with dry granulated zinc and a little zinc-sodium alloy, at first gently, and afterwards at 100°, the reaction being considered as terminated when the product solidifies to a crystalline mass. This is decomposed by adding it in small portions at a time to a mixture of ice and water; hydrochloric acid is added to dissolve the zinc hydrate formed; and the whole is distilled. In the first portions of the distillate oily drops come over along with the water: when this ceases to be the case, the receiver should be changed and the second portion collected, until the addition of solid potassium carbonate no longer causes the separation of any alcohol. The oily layer obtained from the aqueous solution by this means, and consisting chiefly of ethyl alcohol, is dried over potassium carbonate, the alcohol removed by distillation in the water-bath; and the oily residue, after being washed with water, is added to the oil separated from the first portion of the distillate. This crude alcohol is best purified by converting it into the iodide, according to Butlerow's method of passing gaseous hydriodic acid into the alcohol.

The iodide after purification may be re-converted into the alcohol, either by heating it to 130° in a sealed tube with potassium hydrate, or by heating for forty-eight hours with lead hydrate and ten times its volume of water in a flask fitted with a reflux condenser, and standing in a water-bath; distilling the contents to dryness; mixing the distillate with a fresh portion of lead hydrate; heating it under the same conditions, and repeating these operations three or four times. Another method is to heat the iodide with a small quantity of moist silver oxide. In either case, however, a considerable portion of the alcohol is resolved into water and amylene.

The purified alcohol is dried, first over fused potassium carbonate, and then over anhydrous baryta.

Properties and Reactions.—Diethyl-carbinol is a viscid liquid, having the cough-exciting odour belonging to the amyl alcohols in general. It boils at 116°–117°, and has a sp. gr. of 0.832 at 0° and 0.819 at 16°, referred to water at 0°. By careful oxidation with chromic acid mixture it yields, besides acetic and propionic acids, a ketone, $\text{C}^2\text{H}^{10}\text{O}$, which by further oxidation is also converted into acetic and propionic acids.

This reaction, and the easy resolution of the alcohol into amylene and water, as when the corresponding iodide is heated with alcoholic potash, or with silver oxide or lead hydrate and water, shows that this alcohol is a secondary alcohol; and its composition, together with that of the ketone and of the acids formed by the oxidation, shows that it must be either propyl-methyl carbinol, or diethyl-carbinol. The

of formation points to the latter, and it is unlikely that any isomeric change should have taken place during the reaction, since the simultaneous action of zinc-methyl and zinc-ethyl on ethyl formate is found to yield methyl-ethyl carbinol.

Conversion of Diethyl-Carbinol into Propyl-methyl Carbinol.—The diethyl-carbinol was converted by the action of hydriodic acid into the corresponding iodide; half of this iodide was transformed by the action of alcoholic potash into amylene, and this again combined with hydriodic acid. The iodide, $C^4H^{11}I$, thus obtained, and the diethyl-carbinyl iodide, were then treated with lead hydrate and water, and the resulting alcohols were partly converted into chlorides and partly oxidised to ketones. The two alcohols and their derivatives exhibited the properties shown in the following table:—

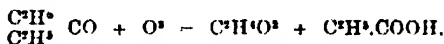
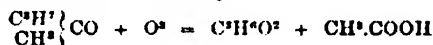
Derivatives of Diethyl-Carbinol.

	B. p.	Spec. grav.	
Iodide, $C^4H^{11}I$	145°–146°	1.528 at 0°	1.501 at 20°
Alcohol, $C^4H^{12}O$	116.5°	0.831 at 0°	0.816 at 18°
Chloride, $C^4H^{11}Cl$	103°–105°	0.916 at 0°	0.895 at 21°
Ketone, $C^4H^{10}O$	104°	0.829 at 0°	0.811 at 19°

Derivatives of the Amylene.

	B. p.	Spec. grav.	
Iodide, $C^4H^{11}I$	144°–145°	1.539 at 0°	1.510 at 20°
Alcohol, $C^4H^{12}O$	118.5°	0.827 at 0°	0.816 at 18°
Chloride, $C^4H^{11}Cl$	103°–105°	0.912 at 0°	0.891 at 21°
Ketone, $C^4H^{10}O$	103°	0.828 at 0°	0.810 at 19°

The differences in the properties of the corresponding compounds are but slight, but those of the amylene-derivatives agree very nearly with those of the propyl-methyl-derivatives (1st Suppl. 112). The two ketones oxidised with chromic acid mixture yield the same products, viz. acetic and propionic acids, as they should do according to Popoff's law (1st Suppl. 765; 2nd Suppl. 711), if the one consists of diethyl ketone and the other of propyl-methyl ketone, thus:—



The transformation of diethyl-carbinol into propyl-methyl carbinol may be explained as follows. Diethyl-carbinyl-iodide, $CH^3-CH^2-CHI-CH^2-OH^2$, is converted by alcoholic potash into the amylene, $CH^3-CH^2-CH=CH-CH^3$. Now when a hydrocarbon containing the group $-CH=CH-$ combines with hydriodic acid, the iodine usually attaches itself to the CH which is nearest to one of the methyl-groups, as is observed in the case of hexylene from mannite. Accordingly the amylene in question should be convertible into the iodide $CH^3-CH^2-CH^2-CHI-OH^2$, which is propyl-methyl iodide (Wagner & Saytzeff, *Liebig's Annalen*, clxxix. 313).

Tertiary Amyl Alcohol, or Dimethyl-ethyl Carbinol, $\begin{matrix} (CH^3)^2 \\ | \\ C^2H^5 \end{matrix} \{ COH$, is formed under certain circumstances, by the action of sulphuric acid on amylene (see the next article).

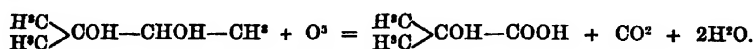
AMYLENE, C^4E^2 . (1.) *Amylenes from Fermentation Amyl Alcohol* (Flavitzky, *Liebig's Annalen*, clxxix. 340).—*a.* Ordinary amylene (b. p. 36°) produced by the action of zinc-chloride at high temperatures on fermentation amyl alcohol, is usually regarded as iso-propyl ethylene, $\begin{matrix} H^2C \\ | \\ CH(CH^3)^2 \end{matrix}$, or $\begin{matrix} H^2C \\ | \\ H^2C \end{matrix} > CH-CH=CH^3$, inasmuch as, on combining it with hydriodic acid, and decomposing the resulting iodide with moist silver oxide, it yields Wurtz's amylene hydrate, which, from its products of oxidation, as observed by Wurtz and by Kolbe (acetic acid, acetone, and isopropyl-methyl ketone), has been supposed to be a secondary alcohol, namely, *isopropyl-methyl carbinol*, $\begin{matrix} H^2C \\ | \\ H^2C \end{matrix} > CH-CHOH-CH^3$ (1st Suppl. 112).

This view of its constitution has however been called in question by Flavitzky (*Liebig's Annalen*, clxxix. 340), who finds that amylene hydrate (prepared by the action of sulphuric acid on ordinary amylene, and boiling at 102.3°), when gradually

oxidised by a solution of chromic anhydride in acetic acid, so as to avoid all energetic action (which might further oxidise any ketones that were formed), yields amylene distilling over below 40°, and acetone between 40° and 60°, but not a trace of methyl-isopropyl ketone, the portion of the liquid which distilled between 60° and 100° consisting almost wholly of unaltered amylene hydrate.

The non-formation of methyl-isopropyl ketone by oxidation of amylene hydrate does away with the only proof that this alcohol is methyl-isopropyl carbinol, inasmuch as a tertiary amyl alcohol, viz. dimethyl-ethyl carbinol, would yield by oxidation acetic acid and probably also acetone.

Neither is the *amylene-glycol* (b. p. 170°) which Wurtz obtained by the action of silver acetate on the dibromide of ordinary amylene, a methyl-isopropyl compound; for when oxidised by dilute nitric acid it is converted in butylactic or α -oxylisobutyric acid, $\begin{smallmatrix} \text{H}^{\text{C}} \\ \text{H}^{\text{C}} \end{smallmatrix} > \text{COH} - \text{COOH}$ (1st Suppl. 891); consequently this glycol must have the structure $\begin{smallmatrix} \text{H}^{\text{C}} \\ \text{H}^{\text{C}} \end{smallmatrix} > \text{COH} - \text{CHOH} - \text{CH}^{\text{C}}$, its oxidation to butylactic acid being represented by the equation :



Ordinary amylene from which this alcohol is derived must therefore be trimethyl-ethylene, $\begin{smallmatrix} \text{H}^{\text{C}} \\ \text{H}^{\text{C}} \end{smallmatrix} > \text{C} = \text{CH} - \text{CH}^{\text{C}}$.

β . An amylene boiling at 25° is formed, together with ethyl-amyl oxide, by the action of alcoholic potash on the iodide obtained by treating fermentation amyl alcohol (active or inactive) with hydriodic acid. The amylene is separated by washing the product with water, drying over calcium chloride, and rectifying several times over sodium. It unites with bromine at ordinary temperatures, forming a bromide, $\text{C}^{\text{H}}_{10}\text{Br}_2$, boiling at 185°–190°; when heated with fuming hydrochloric acid, it yields a hydrochloride, $\text{C}^{\text{H}}_{10}\text{HCl}$, boiling at 85°–86°, and when it is well cooled and a stream of chlorine is passed through it, a product is formed which boils for the most part at 149°. Heated with fuming hydriodic acid in sealed tubes placed in a water-bath, it is converted into a hydriodide, $\text{C}^{\text{H}}_{10}\text{HI}$, boiling at 129°–130°; this compound treated with dry silver acetate, added by small portions, is converted into the corresponding acetate, $\text{C}^{\text{H}}_{10}\text{C}^{\text{H}}_{10}\text{O}_2$, boiling at 124°–125°; and by saponifying this compound with strong aqueous potash, the corresponding amyl alcohol or amylene monohydrate, $\text{C}^{\text{H}}_{10}\text{H}(\text{OH})$, is obtained, as a liquid having the smell and taste of the alcohol obtained from ordinary amylene and boiling at 103°–104°.

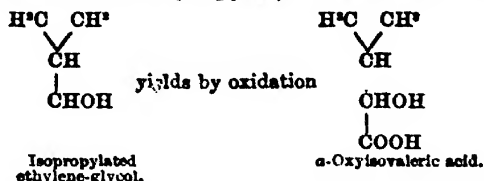
This amylene when gradually oxidised by a mixture of potassium dichromate and sulphuric acid yields the same products as ordinary amylene, viz. acetic acid and acetone, but no methyl-isopropyl ketone. Moreover the monatomic derivatives of the two amylenes are identical in physical properties, as the following table will show :—

	Alcohol. B. p.	Iodide. B. p.	Chloride. B. p.	Acetate. B. p.
From Amylene, b. p. 25° .	103°–104°	129°–130°	85°	124°–124·5°
" " " 35° .	165°	130°	85° (Berthelot) 90° (Wurtz)	125°
	Sp. gr.	Sp. gr.	Sp. gr.	Sp. gr.
From Amylene, b. p. 25° .	0·826	1·521	0·891	—
" " " 35° .	0·826	1·522	—	—

Nevertheless the two amylenes cannot be identical, inasmuch as they differ in their boiling points by ten degrees. Moreover the amylene boiling at 25° yields a glycol differing in all its properties from that which is obtained from ordinary amylene. This glycol was prepared by combining the amylene with bromine, heating the resulting dibromide with silver acetate and glacial acetic acid at the heat of the water-bath, and decomposing the resulting di-acetate with dry potassium hydrate or baryta. The glycol thus obtained is a transparent, colourless, thick liquid, having no smell, but a burning bitter taste, miscible in all proportions with water, easily soluble in alcohol and ether. It boils at 206° (ordinary amylene-glycol at 177°), and has a sp. gr. of 0·9987 at 0°, 0·9843 at 21·5° (ordinary amylene-glycol, 0·987 at 0°).

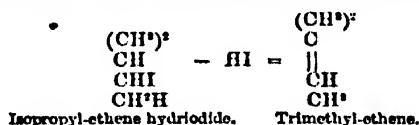
This glycol is converted by oxidation with dilute nitric acid (2 parts strong acid

and three parts water) into α -oxyisovaleric acid (2nd Suppl. 885), and consequently must have the structure of isopropylated ethene-glycol; thus:



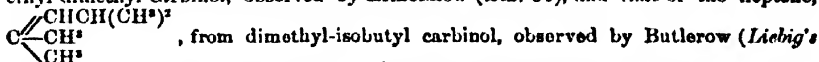
Hence it follows that the amylene boiling at 25° is isopropyl-ethene, $\begin{array}{c} \text{H}^{\text{c}} \quad \text{c} \\ \diagdown \quad \diagup \\ \text{H}^{\text{c}} \end{array} \text{CH}=\text{CH}=\text{CH}^{\text{c}}$.

When this amylene is combined with hydriodic acid, and the resulting hydriodide is decomposed by alcoholic potash, an amylene is obtained boiling at 36° , and agreeing in every respect with ordinary amylene or trimethyl-ethene. Here, then, it is evident that the iodine is removed from the compound, in combination with an atom of hydrogen different from that with which it had combined; thus:—



This conversion of an amylene having a structure analogous to that of a secondary alcohol into another constituted similarly to a tertiary alcohol, is an example of a law which appears to be general, viz. that, in the formation of hydrocarbons of the ethene series, there is a tendency to the production of those modifications which contain the maximum number of methyl-groups.

Other examples of this law are afforded by the transformations of the butyl alcohols observed by Linnemann (2nd Suppl. 217, 219); the conversion of isobutyl bromide by heating to 230° – 240° , into trimethyl-carbinyl bromide, observed by Elkoff (Deut. Chem. Ges. Ber. vi. 258), the formation of trimethyl-ethene from ethyl-dimethyl carbinol, observed by Ermolaiew (*ibid.* 64), and that of the heptene,



Annalen, clxii. 189). This tendency to the multiplication of methyl-groups in an ethene-molecule is probably due to the fact that methyl- is the most stable compound of carbon and hydrogen that can enter into a compound of the fatty series. To the same cause may perhaps be attributed the fact that the normal compounds of the fatty series, which contain the minimum number of methyl-groups, are the most difficult of all to produce synthetically. Ethene itself can hardly be considered an exception in this respect, inasmuch as it belongs to a peculiar type analogous to benzene.

The following hydrocarbons, to judge from their boiling points, are probably also identical with ordinary amylene:

1. Obtained by the action of zinc-amalgam on ordinary amyl iodide (Frankland, *Chem. Soc. Journal*, iii. 35, 44).
2. By the dry distillation of sodium amylate (Mendelejeff, *Lehrb. d. org. Chem.* 1863, 395).
3. By dehydration of ethyl-amyl oxide with phosphoric anhydride (Flavitzky, *Lieb. Ann.* clxix. 206).

Action of Sulphuric Acid on Amylene.—When dilute sulphuric acid of sp. gr. 1.67 at 20° (2 vol., H_2SO_4 , to 1 vol. water) is gradually mixed in a vessel cooled by a freezing mixture with ordinary amylene, an amyl alcohol is obtained, in the form of a colourless liquid, smelling like camphor and bitter almond oil, solidifying at -30° , boiling at 96° – 97° , and yielding an iodide which boils at 115° – 120° ; identical, therefore, with dimethyl-ethyl carbinol (1st Suppl. 115). When, on the other hand, sulphuric acid of sp. gr. 1.545 at 20° (2 pts. by weight of H_2SO_4 to 1 pt. of water), is used instead of the stronger acid, an alcohol is formed which remains liquid at -30° , boils at 102° , 105° , and yields an iodide boiling at 125° – 127° . These are nearly the properties of methylisopropyl-carbinol (*ibid.* 113). Hence it appears that the action of sulphuric acid on amylene may give rise, either to a secondary or to a

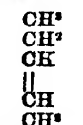
tertiary alcohol, according to the concentration of the acid used (Ossipoff, *Deut. Chem. Ges. Ber.* viii. 542, 1240). Compare Flavitzky (*2nd Suppl.* 64).

When the amylene which boils at 25° is dissolved in sulphuric acid, part of it becomes polymerised to diamylene, identical with that which is obtained in like manner from ordinary amylene (Flavitzky, *Deut. Chem. Ges. Ber.* viii. 767).

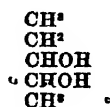
On the Decomposition of Amylene Bromide by the Copper-zinc Couple, see OLEFINES.

(2.) *Amylene from Diethyl-Carbinol* (Wagner a. Saytzeff, *Lieb. Ann.* clxxix. 302).—This amylene (b. p. 38°) is easily formed by heating diethyl-carbinyl iodide with alcoholic potash, or with silver oxide, or lead oxide and water (p. 78). The bromide, formed by pouring bromine in a fine stream into the amylene contained in a flask surrounded by cold water, is a colourless liquid having a sweetish taste, and boiling with partial decomposition at 178° , under a barometric pressure of 758.8 mm. at 0° (bromide of ordinary amylene boils at 170° – 176° ; that of ethyl-allyl at 175° ; that of isopropyl-ethene at 175° – 180°); its specific gravity is 1.7087 at 0° , 1.6868 at 14° (compared with water at 0°); expansion coefficient for 1° between 0° and 14° = 0.00093.

The corresponding glycol, prepared by decomposing the bromide with silver acetate and glacial acetic acid, and heating the resulting acetate with caustic baryta and water, is a viscid syrupy liquid, having a burning rather bitter taste, but no smell. It boils at 187.5° , under a pressure of 759.9 mm. at 0° (Wurtz's amyl-glycol boils at 177° , Flavitzky's at 206°). Its specific gravity is 0.9945 at 0° , 0.9800 at 19° (compared with water at 0°). By oxidation with nitric acid, it is converted into α -oxybutyric acid (1st *Suppl.* 891), formic acid and carbon dioxide, together with acetic and glycollic acids. The formation of α -oxybutyric acid, $\text{CH}_3\text{—CH}_2\text{—CHOH—COOH}$, shows that the glycol and the amylene from which it is derived have the structure represented by the following formulæ:—



Amylene.



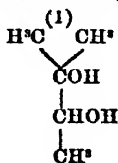
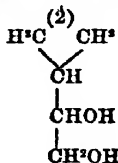
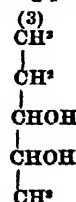
Glycol.

The amylene from diethyl-carbinol is therefore methyl-ethyl-ethene, $\text{CH}(\text{CH}^3\text{CH}^3)$, and its formation completes the group of the four possible amylenes, whose formulæ are given in the *2nd Supplement*, p. 64, the other three being Wurtz's ethyl-allyl, analogous in structure to normal amyl alcohol; isopropyl-ethene, analogous to fermentation amyl alcohol; and trimethyl-ethene, analogous to methyl-isopropyl carbinol.

AMYLENE GLYCOLS, or AMYL GLYCOLS, $\text{C}_5\text{H}_{12}\text{O}_2 = \text{C}_5\text{H}_{10}(\text{OH})_2$.
Three of these compounds are known, viz.:

- (1.) That obtained by Wurtz from ordinary amylene or trimethyl-ethene (i. 208).
- (2.) That obtained by Flavitzky from isopropyl-ethene (p. 80).
- (3.) That obtained by Wagner a. Saytzeff from methyl-ethyl-ethene (*supra*).

The following is a comparative view of their formulæ and boiling points:—

B.p. 177° .B.p. 206° .B.p. 187.5° .

The amylene-glycol derived from normal amylene or ethyl-allyl has not yet been obtained.

AMYLOGEN. Soluble Starch. See STARCH.

AMTLOXYSULPHORENOLIDE. See OXYLSULPHORENOLIDE.

AMYL-PHOSPHINES. See PHOSPHINES.

ANACARDIUM. The nuts of *Anacardium orientale* contain a black fatty matter, which mixes readily with melted wax, stearin, paraffin, &c., and is used for giving a black colour to candles (Böttger, *Dingl. pol. J.* ccc. 490).

ANALYSIS. *Proximate Analysis of Minerals.*—Fouqué (*Compt. rend.* lxxvi. 1089) has given a method of proximate mineral analysis depending on the successive use of a magnet and of hydrofluoric acid. The mineral is reduced to a coarse powder, from which an electromagnet, excited by 6–8 Bunsen's elements, removes all the ferruginous particles, a white powder remaining behind, which contains nothing but the felspathic constituents of the mineral. Strong hydrofluoric acid may be employed to remove the felspathic and vitreous constituents, a powder then remaining, which consists of crystals of pyroxene, peridote, sphene, and oxides of iron, the latter of which may be removed by a weak magnet. The crystals of pyroxene and peridote are sufficiently different in colour to allow of an easy separation with the aid of a magnifying glass.

New forms of apparatus for use in quantitative analysis are described by A. Gawalowski (*Zeitschr. Anal. Chem.* xii. 181; *Chem. Soc. Jour.* [2], xii. 287).

Modifications of the apparatus for Elementary Organic Analysis, by J. Löwe (*Zeitschr. Anal. Chem.* xi. 403; *Chem. Soc. Jour.* [2], xi. 1087). Apparatus for Technical Gas-analysis, by C. Winckler (*J. pr. Chem.* [2], vi. 301; *Chem. Soc. Jour.* [2], xi. 651).

Errors in the ultimate Analysis of Organic Bodies.—G. S. Johnson (*Chem. Soc. Jour.* 1876, i. 178) has drawn attention to two possible sources of error in organic analysis: (1.) From the presence of nitrite in the potash-solution used for absorbing the carbonic acid. In most organic analyses, as now conducted, a stream of oxygen more or less abundant is passed through the potash-bulbs; and if the liquid in these bulbs contains potassium nitrite, this salt will absorb oxygen and be converted into nitrate, and consequently the weight of the bulbs will be increased.

(2.) The copper reduced by hydrogen for decomposing the nitrogen oxides evolved in the combustion of azotised organic bodies, sometimes occludes hydrogen. Now, at the commencement of a combustion, either with lead chromate or copper oxide, the copper becomes blackened on the surface from oxidation; but as the temperature rises, the occluded hydrogen is set free, and reduces the film of oxide on the surface, forming water which passes over into the chloride of calcium tube; hence the weight of this tube may be increased by water not due to the combustion of hydrogen in the substance under analysis.

Volumetric Analysis. Use of Permanganate.—Potassium permanganate is perhaps the most delicate reagent that can be used in volumetric analysis, but its application is sometimes interfered with by the production of coloured compounds, which obscure the exact point of peroxidation. Such is the case when iron is present as ferrous chloride, the yellow colour of the resulting ferric chloride presenting a great obstacle to the exact determination of the limit of the reaction, to such an extent indeed that the use of permanganate in the analysis of iron ores has been almost superseded by that of potassium dichromate. It has lately, however, been shown by E. A. Parnell (*Chem. Soc. Jour.* [2], xiii. 77) that the difficulty above mentioned in the application of permanganate to the analysis of iron compounds may be completely obviated by the use of artificial light. Viewed by candle-light reflected from a white ground, the colour of ferric chloride is so greatly reduced, that a solution containing about 3 pts. ferric chloride (or 1 pt. iron) in 400 pts. water is almost colourless. For further details respecting the use of permanganate in the analysis of iron ores, see IRON, ESTIMATION OF.

Indicators for the Titration of Acids and Alkalis.—1. *Alizarin.*—According to E. Schaal (*Deut. Chem. Ges. Ber.* vi. 1180) alizarin is a much more delicate test for acids and alkalis than litmus, being capable of detecting 1 part of alkali in 300,000, and exhibiting in neutral solutions a distinct yellow colour with 0.0007 pt. of hydrochloric acid. To prepare the test-solution, an excess of alizarin, together with a drop of phenol (to preserve the alizarin from decomposition), is dissolved at boiling heat in potash-ley, and the liquid when cold is filtered from undissolved alizarin. The reaction is the most delicate when the alizarin solution is first supersaturated with acid and then titrated back with alkali. The neutralisation of the acid is complete as soon as the yellow changes to rose-colour, the smallest trace of free alkali being sufficient to produce this effect.

When a solution of alizarin in distilled water is dropped into spring water and warmed, the water becomes red, showing that it is alkaline, and the amount of alkali may be determined without previous concentration.

Strips of paper coloured, on the one hand, with an alcoholic solution of alizarin,

and, on the other, with the above-described neutral solution, may be used for testing instead of red and blue litmus-paper.

2. Phenol-phthalein.—This body, which is easily prepared by heating phenol with phthalic anhydride and sulphuric acid, is perfectly colourless in a dilute aqueous solution, neutral or acidulated, but assumes a deep purple colour on addition of the slightest excess of alkali. One part of phenol-phthalein in 100,000 parts of water is turned red by the smallest trace of alkali, and the coloration is destroyed by the slightest excess of acid. The indicator is prepared by dissolving 1 part of phenol-phthalein in 30 parts of alcohol, and of this solution 1 or 2 drops (not more) are added to 80–100 c.c. of the liquid to be tested. (E. Luck, *Zeitschr. Anal. Chem.* xvi. 332).

3. Logwood.—F. Stolba (*Dingl. pol. J.* ccxvi. 527) recommends logwood as an indicator in volumetric analysis in place of litmus. The logwood is added in small chips, and the operation must be carried out in boiling liquids. The slightest excess of acid changes the colour of an alkaline liquid coloured with logwood from red to yellowish green: conversely, the slightest excess of alkali restores the red colour. For organic acids, however, litmus gives better results. The reaction with logwood is quite distinct by gas-light.

Chlorine may be volumetrically determined in the same liquid which has served for the determination of the alkali, if only a very small splinter of logwood has been used, and the titration has been effected with nitric acid.

ANDESIN. Specimens of this sodio-calcic felspar from Vesuvius, from Monte Mulatto, near Predazzo, and from Orenberg in the Ural, have been described and analysed by G. vom Rath (*2nd Suppl.* 512, 513).

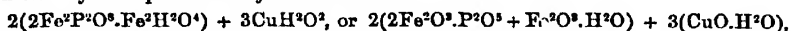
ANDESITE. On the Quartziferous Andesites in Hungary and Transylvania, see Doelter (*Jahrbuch f. Mineralogie*, 1873, 772). On Andesite containing Augite and Hornblende from Toplitia, near György St. Miklos in Transylvania, see K. John (*ibid.* 1874, 646; *Chem. Soc. Jour.* [2], xiii. 550).

ANDREWSITE. A mineral from Cornwall, occurring in globular and occasionally discoid forms, having a radiated structure like that of wavellite, and a dark green colour, with a somewhat glaucous cast; streak green; hardness = 4; sp. gr. = 3.475.

An analysis (by Flight) of andrewsite, freed as completely as possible from a brown mineral forming the nucleus of the globules, gave

Fe ² O ³	Al ² O ³	FeO	CuO	P ² O ⁵	H ² O	MnO	CaO	SiO ²
44.64	0.02	7.11	10.86	26.09	8.79	0.60	0.09	0.49 = 99.59

which may be represented by the formula:



supposing the sample analysed to have contained about one-third of an equivalent of limonite, and a small amount of silica proceeding from admixed veinstone.

Andrewsite in many respects resembles dufrénite, $\text{Fe}^2\text{P}^2\text{O}^6 \cdot \text{Fe}^2\text{H}^2\text{O}^4$, but differs from it in containing a considerable quantity of copper.

The globules of andrewsite are occasionally studded with brighter green crystals of chalcosidite, which sometimes also encrusts the andrewsite with a thin surface layer. The interior of the globules is sometimes nearly homogeneous throughout, consisting of radiating crystalline fibres or minute prisms, but they more frequently contain a core of a brown mineral much resembling xanthosiderite, and giving by analysis—

Fe ² O ³	P ² O ⁵	H ² O	SiO ²	CaO	CuO
73.92	12.28	7.85	1.48	4.31	trace = 99.84.

Regarding the first three ingredients as the true constituents of the mineral, and a small amount (about $\frac{1}{2}$ mol.) of ferric oxide as forming ferruginous quartz with the silica, the preceding numbers may be represented by the formula $\text{Fe}^2\text{P}^2\text{O}^6 + 2\text{Fe}^2\text{H}^2\text{O}^4 + \text{Fe}^3\text{H}^2\text{O}^4$, or a mol. of ferric orthophosphate associated with 2 mol. goethite and 1 mol. limonite.

The variation in character presented by the interior of the globules containing this brown core seems to have resulted from a decomposition proceeding from the interior outwards. In this case the spherical andrewsite is often associated with crystals of cuprite, and deposited upon sprigs of native copper, round which, as a nucleus, it seems to have been formed.

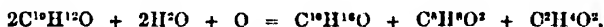
The veinstone on which andrewsite occurs is a highly ferruginous quartz, generally covered with limonite, which again is frequently encrusted with a thin coating of velvety goethite (Maskelyne, *Chem. Soc. Jour.* [2], xiii. 586).

ANETHOL. $\text{C}^{10}\text{H}^{12}\text{O}$. The following derivatives of anethol have been prepared and examined by Landolph (*Compt. rend.* lxxxi. 97; lxxxii. 226).

Anethol Hydride or *Anise Camphor*, $C^{10}H^{14}O$.—Commercial anise-oil yields, after several rectifications, about 90 per cent. of pure anethol boiling at 226° . To transform this substance into anisaldehyde, about 50 grams of it are boiled for an hour with 300 grams of nitric acid of 13° B., and the product washed, first with water, then with dilute soda. The oily body thus obtained amounts, when distilled, to about 20 per cent. of the anethol employed, and is a mixture of anisaldehyde and anise camphor, in about equal proportions. This is agitated with sodium-hydrogen sulphite, and the crystalline body produced is washed with mixed alcohol and ether till it is perfectly white.

The portion of the oily body uncombined, obtained from the alcohol and ether washings, yields, when purified by distillation, a product boiling at 190° – 193° , of camphorous odour, liquid, and lighter than water. This is anethol hydride, or anise-camphor, isomeric with common laurel-camphor. When oxidised with potassium bichromate and sulphuric acid, it yields an acid which crystallises in long needles, melting at 175° , and exhibiting the properties of aniseic acid.

The formation of anisaldehyde and anise-camphor from anethol is represented by the equation:



the oxidation being attended with fixation of water.

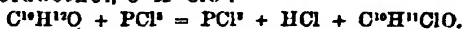
When anethol hydride is heated in a closed vessel to 185° for twenty-four hours with *alcoholic potash* of 10° B., the product treated with water, and the insoluble portion taken up with ether, a viscid, perfectly limpid liquid is obtained, having the composition $C^{10}H^{14}O$, which is that of a campholic alcohol isomeric with Borneo camphor. This substance has a very characteristic odour resembling that of mould. It is lighter than water, boils at 198° , and crystallises easily at 0° in slender radiate needles, melting at 18° – 19° . It is not dissolved by potash.

Products of Condensation.—The essential oil, in portions of 4 to 5 grams, is heated to 185° for eighteen hours with alcoholic potash of 10° B., the alcohol removed by distillation, and the residue treated with water. The anethol unacted upon is removed by ether; and the aqueous solution is treated with hydrochloric acid and extracted with ether, which is then evaporated off, and the residue distilled in the vapour of water. One product, which is crystallisable, passes into the receiver; another, which is resinous, remains in the retort. The former is easily soluble in alcohol, ether, and benzene, which, on evaporation, leave it as a heavy oil; and slightly soluble in hot water, which, about thirty-six hours after cooling, deposits it in monoclinic plates, melting at 87° , and having the composition $C^{12}H^{18}O^2$, which is that of an isomeric of the ethylic ether of aniseic alcohol.

The *acetyl-derivative* of this compound is easily obtained by heating it to 100° for six hours with acetic anhydride. It is viscid and easily decomposed by heat. Its composition is represented by the formula $C^{12}H^{22}O^2$, which is that of a diacetic ether of a diphenol.

The resinous body which accompanies the crystalline substance above-mentioned always forms at least one-half of the entire product, and if the action be prolonged, and especially if the concentration of the alcoholic potash be increased, may even constitute the sole product of the reaction. It melts at 65° , and has the composition $C^{14}H^{20}O^2$. Heated with acetic anhydride it is converted into a monacetic ether, $C^{14}H^{20}O^2$, or $C^{14}H^{18}(C^2H^3O)O^2$. It has a yellowish-red colour, yields a nearly white powder, has a very pleasant odour, and melts at about 40° .

Action of Phosphorus Pentachloride on Anethol.—When anethol is heated for five or six hours with a slight excess of phosphorus pentachloride, a reaction takes place, attended with only a slight evolution of hydrochloric acid; but on subsequently heating the liquid over an open fire, torrents of that gas are given off, and a liquid is obtained which, after repeated rectification and washing with dilute soda-ley, has the composition of monochloranethol, $C^{10}H^{11}ClO$:



This compound boils at 228° – 230° , burns with a smoky flame, has a pungent though moderately agreeable odour. Sp. gr. = 1.191 at 20° (that of anethol at the same temperature is 0.984). Exposed to a freezing mixture, it solidifies to a crystalline mass which melts at -4° to -3° .

Monochloranethol is readily attacked by *alcoholic potash*, yielding two products of condensation, analogous to those which are obtained with anethol itself. The chief product, insoluble in water and in potash, is a limpid, slightly oily liquid, having a very agreeable, ethereal, though slightly musty odour, like that of the product of transformation of anethol hydride. It boils at 268° – 270° , and does not solidify at -35° . Its composition is represented by the formula $C^{14}H^{20}O^2$.

The second condensation-product, soluble in potash, is a liquid phenol very difficult to purify, and yielding a solid potassium salt. The first-mentioned condensation-product is completely transformed into the phenol by repeated treatment with alcoholic potash.

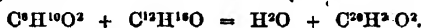
Products of Reduction, and Constitution of Anethol.—To obtain the hydrocarbons corresponding with the chief radicles in anethol, Landolph heated it with amorphous phosphorus and hydriodic acid of sp. gr. 1.72 to 260° for twenty-four hours (3 parts anethol, 2 of phosphorus, and 25 of hydriodic acid). In this way, from 80 grams of pure crystallisable anethol distilling at 228°–230°, there were obtained 40 of a hydrocarbon distilling at 80°–250°, and 10 passing over at above 300°, after washing with dilute sulphurous acid to separate free iodine. By fractional distillation an octene and a hydrocarbon of composition $C^{12}H^{22}$ were separated from the former portion, boiling respectively at about 150° and 210°–212°, after separation of traces of benzene by means of cold fuming nitric acid, and reduction of the resulting nitro-compounds with tin and hydrochloric acid. The octene had the vapour-density 3.91, calculated 3.87, whilst the other hydrocarbon gave 5.70, calculated 5.73.

The unsaturated hydrocarbon, $C^{12}H^{22}$, combined directly with bromine, and was present to the extent of rather more than one-third of the total hydrocarbons formed during the reduction, the octene forming about one-third. The gas liberated was almost pure hydrogen, containing not more than two or three per cent. of a hydrocarbon, probably benzene or hexene, or possibly ethane or methane.

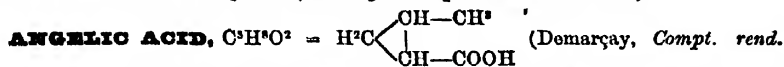
The chief action of hydriodic acid on anethol may therefore be represented by the equation :



Hence Landolph concludes that the formula of anethol should be doubled (notwithstanding its vapour-density, which corresponds with the C^{10} formula), and that the body may be regarded as formed from a hypothetical aldehyde (acecampholic aldehyde), $C^{12}H^{10}O$, which is itself derived from the unknown acetylene oxide, C^2H^2O , and campholic aldehyde, C^8H^8O , by elimination of H^2O . By union with anisic alcohol, $C^8H^{10}O^2$, and elimination of H^2O , this hypothetical acecampholic aldehyde gives rise to anethol, thus—



Anethol is thus regarded as a kind of acetal: this view of its constitution is in harmony with the results above described, whereby it was shown that, on oxidising anethol by nitric acid, there are obtained equal quantities of anisic aldehyde, $C^8H^8O^2$, and anisic camphor, $C^8H^{10}O$, with a certain amount of acetic acid; *i.e.*, it is made up of a C^8 , a C^{10} , and a C^2 compound (Landolph, *Compt. rend.* lxxxiii. 849).

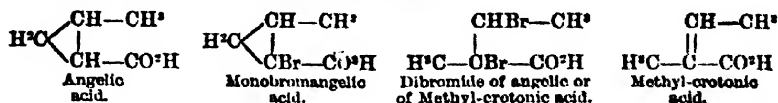


lxxx. 1400). This acid, treated with bromine, is converted into a dibromide, $C^8H^8Br^2O^2$, isomeric with dibromovaleric acid, the solution of which in potash deposits when heated an oil having the composition of monobromobutylene, C^4H^5Br (*1st Suppl.* 157), and sometimes, under conditions not yet determined, gives rise to the production of an acid isomeric with angelic acid, which is more easily prepared by distilling the dibromide of angelic acid. This distillation yields a large quantity of gas, and an oil which sometimes solidifies in crystals; and on dissolving this oil in potash, heating it to the boiling point, separating it from a small quantity of a brominated liquid, and treating it with sulphuric acid, the above-mentioned isomeric acid of angelic acid is deposited as an oil which quickly crystallises. The crystals, purified by distillation and by repeated pressure between bibulous paper, are colourless, have a faint odour recalling that of angelic acid, dissolve very sparingly in cold water, more freely in boiling water, the solution on cooling depositing the acid in a mass of small shining needles. This acid melts at 61°–62°, and boils at about 194°–198°, but the boiling point rises a little towards the end. Its ethylic ether boils at 153°–155°, and has a sweet smell like that of angelic ether.

In all these characters, except the odour of the ether, the acid in question agrees with Frankland's methyl-crotonic acid (*1st Suppl.* 828), and its identity with that acid is shown by the fact that, when fused with potassium hydrate, it is resolved into acetic and propionic acids. The repulsive odour ascribed by Frankland to the ethylic ether of methyl-crotonic acid may perhaps have arisen from a trace of the phosphorous chloride which he used in preparing it.

The dibromide of methyl-crotonic acid is identical with that of angelic acid (the former was found to boil between 79° and 82°; the latter between 77° and 80°), the two acids yielding the same products by solution in potash and by dry distillation.

This identity may be explained by supposing that bromine, in acting upon angelic acid, first takes the place of an atom of hydrogen situated near the group COOH (as it does in many other cases) and that the hydrobromic acid thereby formed unites with the resulting monobrominated acid, thus—



ANGLESITE. *Native Lead Sulphate.*—This mineral occurs associated with galena in the Castle Dome district of Arizona (U.S.). The unoxidised galena sometimes forms a nucleus, but in other cases it has entirely disappeared, the anglesite being arranged in continuous elliptical or circular bands similar to those sometimes seen in agate. The transition in colour, due to the progressive oxidation, from the central black galena to the greyish-white or colourless and transparent anglesite, is often very gradual. The sp. gr. of the light variety is about 6, while in some of the dark varieties it is 6.44. Hardness = 3. Analysis showed that a specimen might be dark and yet contain but 0.2 per cent. less lead sulphate than the light variety, the mean amount being 98.83 per cent. The difference in colour is due to the remaining 1 per cent., which in the dark specimens is made up almost entirely of lead sulphide, while in the light variety it is chiefly clay. The anglesite contains only half as much silver as the galena (Brush, *Sill. Am. J.* [3], v. 421).

Anglesite is also found at Langenstrigis, sometimes in imperfectly developed crystals, sometimes in fine crystals exhibiting three distinct types. The commonest forms are horizontally prismatic crystals of the combination $\{P \infty P\}$. The crystals of the second type are pyramidal through P and an acuter pyramid, probably $2P$; these pyramids occur either independently or else in combination with the prism ∞P . The crystals of the third type are the largest and finest; they are prismatic parallel to the vertical axis, and exhibit the combination $\infty P \cdot \infty P_2 \cdot \infty P \cdot \infty OP$. (Frenzel, *Jahrb. f. Min.* 1875, 685).

ANGUSTURA BARK. When thin transverse sections of true *Angustura bark* (*Cusparia febrifuga*) are examined under the microscope, and compared with sections of the false bark (from a species of *Strychnos*), both being moistened with glycerin, irregularly scattered cells will be observed in the true bark, whereas the false bark presents two zones of sclerogenous cells, entangled with one another. When the sections are moistened with water, cells containing calcium oxalate are seen in the true bark, but they are absent in the false bark. When true *Angustura bark* is moistened with nitric acid, a granular substance, supposed to be cusparin, melts in each cell, with disengagement of gas, into a red liquid, which finally disappears with excess of acid; but in the false bark the coloration spreads through the tissue.

When a thin section of the suberous layer of false *Angustura bark*, first treated with nitric acid, is immersed in glycerin, the cells are observed to be rounded, empty, and coloured emerald-green on the sides; this appearance is not observed in the suber of true *Angustura bark* (P. Cazeneuve, *Pharm. J. Trans.* [3], v. 7). c.

ANILINE. See AMIDO-BENZENE, under BENZENE.

ANILINE COLOURS. Estimation by means of *Sodium Hyposulphite*.—When an aqueous solution of magenta or other aniline colour is mixed with a solution of sodium hyposulphite (Schützenberger's hydrosulphite, 1st Suppl. 1863), the aniline salt is instantly reduced, and the solution decolorised. This reaction may be utilised for the estimation of the tinctorial power of the various coloured aniline-derivatives.

The strength of the hyposulphite solution is ascertained by titrating it against a known weight of the pure crystallised aniline colour, after which it is used as an ordinary volumetric solution; some care, however, is required in the manipulation of this reagent, owing to the rapidity with which it absorbs oxygen. The operations must be conducted in a closed vessel, from which the air has been expelled by a current of carbonic anhydride, and since the decolorisation takes place only at 100° , the liquids under examination must be raised to the boiling heat.

One molecule of the various aniline colours, whose composition is accurately known, requires for complete decoloration the same quantity of hyposulphite as that which is required to reduce two molecules of ammoniacal copper sulphate. From this circumstance it is possible, if the law obtains universally, to deduce approximately the molecular weight of any well-defined aniline colour. Thus the 'violet de Paris' and Hofmann's violet gave absolutely identical results; the molecular weight of the 'violet de Paris' was found to be 460, a number which corresponds very well with the

formula, $C^6H^4(CH^3)N^{\cdot} \cdot 2(CH^2Cl) + H^2O = 462$, analogous to that of 'iodine green' (1st Suppl. 163), A. Stann (*Bull. Soc. Chim.* [2], xix. 124).

On the Impurities and Adulterations of Aniline Blue, Green, Violet, Yellow, and Orange, see Springmühl (*Chem. Centr.* 1873, 140, 207, 220, 761, 762; *Chem. Soc. Jour.* [2], xii. 611, 612, 834, 835).

On the Appearances presented by certain Aniline Colours when diffused on the surface of Water, see Obermeyer (*Pogg. Ann.* cli. 130; *Chem. Soc. Jour.* [2], xii. 1044).

Fixing of Aniline Colours.—The power possessed by silk and wool of fixing these colours directly, whereas vegetable fabrics require previous mordanting with albumin, is attributed by Jacquemin (*Compt. rend.* lxxviii. 1306) to the nitrogen contained in the animal substances. He finds that gun-cotton is dyed directly in solutions of fuchsine or of aniline blue, without any diminution of its combustibility.

Aniline green, however, appears to possess but little affinity for wool, and therefore requires a mordant. For this purpose C. Lauth (*Bull. Soc. Chim.* [2], xix. 401) proposes the use of electro-positive sulphur precipitated from a bath of sodium thio-sulphate containing a little alum, by the addition of an acid; sulphur deposited from its solution in carbon sulphide, or precipitated from the polysulphides by an acid, does not answer the purpose. The wool, before mordanting, should be cleansed, and treated with dilute hydrochloric acid to remove any metallic salts, which would otherwise give a brown shade, from formation of metallic sulphides. It is dyed in the usual way in a solution of the green in hot water; the shade can be rendered more or less yellow by the use of picric acid, adding to the bath at the same time some acetate of zinc or acetate of soda, accordingly as a yellow or a blue green is required. Mixed fabrics of wool and cotton can be dyed by mordanting first with sulphur and then with sumach.

On the use of Size containing Tannic Acid for fixing Aniline Colours, see *Dingl. pol. J.* ccviii. 397; *Chem. Soc. Jour.* [2], xi. 1276.

On an Aniline Colour for Printing on Cotton Goods, see *Dingl. pol. J.* ccv. 150.

On the use of Aniline Colours dissolved in Collodion for colouring Glass, Paper, &c., see Springmühl (*Dingl. pol. J.* ccv. 277; *Chem. Soc. Jour.* [2], xi. 207).

Aniline Black. *Formation by means of Vanadium Salts, and Theory of its Production.*—When vanadious chloride or ammonium vanadate (1 cgm.) is added to a solution of aniline hydrochloride (8 grams) and potassium or sodium chlorate (3·5 to 4 grams) in 100 grams of water, the liquid darkens at once, and after forty-eight hours the whole of the aniline is converted into aniline-black, the liquid appearing almost solid. Even 1 part of vanadium is sufficient to convert 1,000 parts of aniline hydrochloride into the black. This peculiar action of vanadium is easily explained, as there is no metal which passes more easily than vanadium from a higher state of oxidation to a lower one, and *vice versa*. Thus, if the pentoxide is dissolved in hydrochloric acid, it is converted into vanadious chloride, and on evaporating this solution in the air the pentoxide is reproduced. On the other hand, vanadious chloride and potassium chloride act on each other, chlorine being evolved, and the vanadium being converted into the pentoxide, while if this oxide or a vanadate comes in contact with aniline hydrochloride, it is reduced to a vanadious compound. In the mixture of aniline-black these reactions take place in quick succession.

This mode of action shows that for the production of aniline-black only those metals are available which form more than one oxide or chloride, and moreover that these oxides or chlorides must be readily convertible one into the other. Thus stannous chloride cannot be used, and may even be employed to retard the formation of the black by vanadium, the colour being produced only after all the stannous salt is converted into stannic salt. The salts of iron, cerium, and manganese act similarly to vanadium, while those of nickel, cobalt, and chromium act but slowly, but on adding a little of a vanadium salt the action goes on much more quickly. The salts of the lower oxides of uranium, tungsten, and molybdenum give also good blacks, but the uranic salts act as little as the tungstates and molybdates. The black produced by vanadium is identical with that obtained by copper, and contains no metal, the black being the result of the action of chlorine or its lower oxides on aniline, and is nothing but *dehydrated emeraldine*, the latter losing its water not only on ageing, but also, like hydrated copper oxide, on immersion in a hot liquid. Pure toluidine is by the same reactions converted into toluidine-bronze, and the common aniline-black is a mixture of this body with dehydrated emeraldine.

The reaction above described may be used for the detection of aniline. For this purpose the solution under examination is concentrated with an excess of hydrochloric acid, and a drop of a solution of vanadious chloride is added, which will at once produce the black; on the other hand, aniline may be used as a test for vanadium, the solution

being mixed with hydrochloric acid, potassium chlorate, and aniline hydrochloride; if the black forms rapidly, the presence of vanadium may be safely inferred.

On adding a drop of a vanadium solution to a solution of logwood extract and potassium chlorate, a yellow body is formed dyeing on silk a splendid golden-yellow. By the same reagents, starch, gum, and isinglass are converted into yellow, transparent substances (A. Guyard, *Bull. Soc. Chim.* [2], xiv. 58). See also Rosenstiehl, *ibid.* 356; *Chem. Soc. Jour.* 1878, ii. 316.

In the preparation of thickened colours for printing, the quantity of vanadium employed for the formation of aniline-black should be very small in comparison with the weight of aniline-salt employed, a quantity not exceeding $\frac{1}{50000}$ to $\frac{1}{500000}$ of the weight of aniline hydrochloride being sufficient for the purpose. The use of vanadium instead of copper in this process has the following advantages:—

1. Improvement in the richness of the black, and clearness of the impression.
2. Avoidance of the attacking of the rollers.
3. Facility of regulating the duration of the oxidation.
4. Lengthened preservation of the thickened colours.
5. More simple and economical preparation. It is estimated that the cost for vanadium should not exceed one-eleventh of that for the copper hitherto employed (G. Witz, *Compt. rend.* lxxxiii. 348).

According to Kruis (*Dingl. pol. J.* cccxii. 347), the black obtained by the use of cerium salts exceeds all other aniline-blacks in depth and brilliancy, and a very small quantity is sufficient for its production.

According to Rosenstiehl (*Compt. rend.* lxxxii. 1257) aniline-black may be formed on tissues by the agency of active oxygen alone, without the use of chlorates and metallic substances, if the condition of steaming be not insisted on.

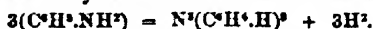
Formation by Electrolysis.—A galvanic current passed through a solution of the hydrochloride, sulphate, or nitrate of aniline causes a deposit on the positive pole, of a colouring-matter, which is green at first, but afterwards becomes violet, and finally deep indigo. Aniline tartrate, oxalate and acetate, do not yield this colour, but give only a brown deposit. When the aniline-salt is completely decomposed, the solution is colourless. The negative electrode becomes black, and a slight black deposit is thrown down in the liquid.

The deposit on the positive pole, after purification, is a beautiful black metallic-looking, crystalline body. It cannot be sublimed, and is insoluble in water, alcohol, and benzene; it is not altered by boiling dilute acids, except by strong acetic acid, which turns it green. It can neither be oxidised nor reduced, and is not attacked by any ordinary reagents. It is changed by boiling with alkalis, for after the action a blue colouring-matter may be extracted with alcohol, which is turned green by ammonia and yellow by acids. It dissolves in strong sulphuric acid with a violet, blue, or green colour, depending on the energy of the action. Water added to this solution produces a green precipitate; and the filtrate from this precipitate contains a red body, the alcoholic solution of which gives a rose colour with ammonia, showing fluorescence like naphthalene-red. The green precipitate, when treated with caustic potash, becomes deep blue, and is decolorised by nascent hydrogen.

The black electrolytic deposit contains nitrogen. It has a more intense black colour than commercial aniline-black (Goppelsroeder, *Compt. rend.* lxxxii. 331). See also Coquillon (*ibid.* lxxxi. 408; *Chem. Soc. Jour.* 1876, i. 266).

Composition of Aniline-Black.—The black prepared by electrolyzing an aqueous solution of pure aniline hydrochloride, and purified by successive treatment with water, alcohol, and ether, gave, as the mean of eleven analyses: carbon 71.366; hydrogen 5.241; nitrogen 15.327; Chlorine 8.941. These results agree with the formula, $C^9H^{11}N^2Cl$, and accordingly this black may be regarded as a chloride, the base of which is the tetramine $C^9H^{10}N^4$, which, like other polybases of the aromatic series, readily forms monobasic salts (Goppelsroeder, *Compt. rend.* lxxxii. 1392).

Nietzki (*Deut. Chem. Ges. Ber.* ix. 616) has analysed aniline-black prepared by heating an aqueous solution of aniline hydrochloride, potassium chlorate, copper sulphate, and ammonium chloride. The product was purified by dissolving it in aniline, precipitating with hydrochloric acid, and boiling the dried precipitate with alcohol and dilute hydrochloric acid. It gave on analysis numbers agreeing approximately with the formula $C^9H^{10}N^2.HCl$. Assuming this to be its true composition, aniline-black may be regarded as the hydrochloride of a base formed as follows:—



A body thus constituted must contain three replaceable atoms of hydrogen.

* The base of this salt agrees in percentage composition with that analysed by Goppelsroeder.

Attempts to introduce ethyl or methyl into aniline-black have hitherto failed, but on boiling the free base with aniline, it undergoes a remarkable alteration, and afterwards gives up to alcohol a bluish-purple substance, the hydrochloride of a new base, the composition of which has not yet been determined.

Aniline-black heated in the water-bath with fuming sulphuric acid, is converted into a sulphonic acid, which dissolves with dark-green colour in water, and forms with alkalis ink-like solutions, from which acids precipitate it in greenish-black flocks. The salts of this acid have not been obtained in the crystalline state (Nietzki).

On the Dyeing of Wool with Aniline-black, see *Dingl. pol. J.* cxx. 153.

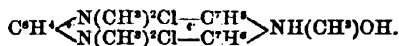
On the Combination of Aniline-black with other Colours on Cotton, see Kiemeyer (*Dingl. pol. J.* cxxvi. 361; *Chem. Soc. Jour.* 1876, i. 816).

Blue Colour produced from Aniline-Black.—When aniline is heated with aniline-black, a blue colouring matter is formed, which is obtained pure by boiling the crude black with alcohol, and treating the residue with soda to obtain the base, which is converted into the acetate by moistening it with acetic acid. The dry acetate is heated with 8–10 times its weight of aniline to 160°–180° for 6–8 days. The product is then treated with an excess of dilute hydrochloric acid, which does not dissolve the hydrochloride of the new base. The latter is obtained in the free state by the action of soda, and purified by dissolving it in ether, precipitating this solution with hydrochloric acid, and repeating this process. The free base, which has either the formula $C^{10}H^{13}N^5$ or $C^{10}H^{11}N^5$, but probably the former, dissolves in ether with a magenta-red colour.

$C^{10}H^{13}N^5.ClH$ crystallises from hot alcohol in needles having a coppery lustre, while, by precipitating the ethereal solution of the base with hydrochloric acid, it is obtained as a crystalline violet powder with little lustre.

$C^{10}H^{13}N^5.IH$ is a very similar compound, and $C^{10}H^{13}N^5.C^6H^5(NO^2)^2O$ is obtained as a crystalline precipitate by adding an aqueous solution of picric acid to an alcoholic solution of the hydrochloride. $(C^{10}H^{13}N^5.ClH)^2PtCl_4$ is a violet crystalline precipitate, sparingly soluble in alcohol, insoluble in water (Nietzki, *Deut. Chem. Ges. Ber.* ix. 1168).

Aniline-Green. Appenzeller (*Deut. Chem. Ges. Ber.* vi. 965) has examined an aniline-green, manufactured by Binscheider and Basch in Basel, and occurring in commerce in splendid crystals, which are readily soluble in water, and are distinguished by the purity and richness of their colour. It has the composition $C^{20}H^{14}(CH^3)^3Cl^2N^4.H^2O + ZnCl_2$, being a double salt of zinc chloride and an aniline-green which differs from Hofmann's and Girard's iodine-green only by containing chlorine in place of iodine (*vert de Paris*, p. 87). When treated with silver nitrate it is converted into a nitrate of analogous composition, which has the same green colour. The chlorine-compound dissolves in acids with a yellowish-brown colour, but the original green is restored on adding a large quantity of water. The water contained in the crystals is given off only when the compound is left in a vacuum for a considerable time, and must therefore be regarded as constitutional water. The constitution of the compound may accordingly be represented by the formula:



On the Fixing of Aniline-green, see p. 88.

On the Dyeing of Straw with Aniline-green: Hartmann (*Dingl. pol. J.* cxxi. 246; *Chem. Soc. Jour.* [2], xi. 305).

Aniline-Grey. A very fine grey is produced on cotton fabrics by printing with a colour prepared by dissolving 625 grams of potassium chlorate in 3½ litres of boiling water, and stirring into the liquid, after cooling, 6½ litres of gum-water, 1312.5 grams of sal-ammoniac, 1500 grams of potassio-chromic tartrate of 30° Baumé, 200 grams of aniline, and 1160 grams of tartaric acid. The whole is well stirred up, the salts then dissolving completely. The potassio-chromic tartrate is prepared by dissolving 960 grams of potassium dichromate in 3 litres of warm water, cooling the liquid to 35° R. (43.75° C.), and stirring into it 1440 grams of finely pulverised tartaric acid (alcohol or sugar might make a cheaper reducing agent). The printing should proceed continuously, and not stop until the last piece leaves the dry plates. The pieces are then hung up for 48 hours in a warm room (temperature about 32° C.); washed and rinsed for an hour, then dried and finished. Light shades may be produced by dilution with gum-water (E. Läubler, *Dingl. pol. J.* ccxi. 490).

Aniline-Red. A new aniline dye of a fine purple-red colour has been prepared by adding ammoniacal cupric hydrate to aniline acetate, then saturating with sul-

phuric acid, and removing the ammonium sulphate by crystallisation (E. Ferrière, *Compt. rend.* lxxvii. 646).

ANILINE TAILINGS, BASE OBTAINED FROM (C. L. Jackson, *Deut. Chem. Ges. Ber.* viii. 968). By distilling a quantity of high-boiling aniline oils, from the factory of Martins and Mendelashon-Bartholdy, in Rummelsburg, a dark tarry fluid was obtained as the last portion. This was dissolved in warm hydrochloric acid, and the solution diluted with water, and filtered through several wet filters, to remove dark oils. After evaporation, caustic soda set free an oil, beginning to boil at 220°, but soon passing over at a temperature above the limit of the mercurial thermometer. The lower fractions consisted of xylydine and its homologues, whilst the fraction boiling at 280° to 320°, furnished with dilute sulphuric acid, the difficultly soluble sulphate of naphthylamine, and a black oil, which was separated from the salt by washing with alcohol. The alcoholic solution, when concentrated by evaporation, deposited the oil, which became a crystalline mass on treatment with strong nitric acid; this was purified by solution in water, precipitation by strong nitric acid, and finally by crystallisation from alcohol. The salt thus obtained had the composition of the nitrate of a base, $C^{12}H^{11}N$, or $C^{12}H^{11}.NH^2$. The free base is precipitated in white flakes when a solution of the nitrate is treated with caustic soda; it dissolves in alcohol and ether, being regained from the solutions thus formed as a brown oil; with chloroform and alcoholic potash it gives an odour like that of phenyl isocyanide, whence it is a primary amine.

The nitrate crystallises in white stellate needles, which are difficultly soluble in water, but more readily in alcohol, and insoluble in nitric acid. Treatment with excess of nitric acid converts it into a red mass resembling rosaniline, from which it is difficult to obtain the salt quite white. The sulphate crystallises in round aggregates of white needles, and is very soluble in water. The hydrochloride crystallises from a slightly acid aqueous solution in long, flat, white needles, soluble in water and in alcohol, and almost insoluble in strong hydrochloric acid; its neutral solution becomes somewhat decomposed on heating. The platinochloride, $2(C^{12}H^{11}N.HCl).PtCl_4$, forms fan-like groups of clear-yellow needles, half a centimeter long; it is slightly soluble in water, more so, though yet sparingly soluble, in alcohol. The alcoholic solution decomposes when heated.

On treatment with acetyl chloride, the base forms an acetyl-derivative, $C^{12}H^{11}.NH.C^2H^3O$, crystallising in white needles which melt at 114.2°; it is insoluble in water, but readily soluble in alcohol and ether.

The base is probably amidophenyltoluene, $C^{11}H^9\left\{\begin{smallmatrix} C^6H^5 \\ NH^2 \end{smallmatrix}\right.$; but the quantity obtained was not sufficient for the exact determination of its constitution.

ANISSETAINE. See BETAINE (2nd Suppl. 188).

ANKERITE. This name is given to a group of carbonates, approaching very nearly to bitter spar, but differing therefrom in respect of their high percentage of ferrous carbonate. Their general formula is $\frac{(Ca,Fe)C^2O^4}{x(Ca,Mg)C^2O^4}$, x having ten different values. Normal ankerite has the formula $\frac{(Ca,Fe)C^2O^4}{(Ca,Mg)C^2O^4}$, and normal paran-

kerite is $\frac{(Ca,Fe)C^2O^4}{2(Ca,Mg)C^2O^4}$. These minerals are found in the coal-formation of Bohemia; normal ankerite also at Kull in the Eifel (Boriky, *Jahrb. f. Min.* 1876, 660). Compare, i. 307; 1st Suppl. 175.

ANORTHITE, $CaAl_2Si_2O^8$ or $CaO.SiO^2 + Al_2O^3.SiO^2$. This mineral occurs, together with monticellite, on the Pesmeda Alp on Mount Monzoni in Tyrol. Its occurrence there is very remarkable, as it has not hitherto been found on the Alps in well-defined crystals, and its occurrence in contact-strata is confined to a few localities, e.g., as so-called amphotelite at Logo in Finland. The crystals of anorthite, which attain a size of 20-25 mm., have an unusual appearance, which renders their determination very difficult. Many of them have a large number of faces; others exhibit the combination $3P.2\bar{P}.\infty.\infty.P.P.$. Distinct twins have not been observed. Of the two following analyses (1) is of flesh-coloured, fresh anorthite, accompanied by chabasite; sp. gr. = 2.686; (2) white, somewhat weathered; sp. gr. = 2.812.

	CaO.	Al ₂ O ₃ .	CaO.	H ₂ O.
(1.)	41.18	35.55	19.65	2.77 = 99.15
(2.)	40.37	35.51	21.58	4.66 = 101.90

(G. vom Rath, *Jahrbuch f. Mineralogie*, 1875, 416).

On the Crystalline Form and Twin-laws of Anorthite, see G. vom Rath (*Pogg. Ann.* cxlvii. 22-63; *Jahrbuch f. Mineralogie*, 1873, 78).

ANTHOLITE or **ANTHOPHYLLITE**. This variety of hornblende (iii. 169) has been found at Star Rock, Concord, Delaware, exhibiting the following composition:—

SiO ² .	Al ² O ³ .	FeO.	MnO.	CaO.	MgO.	Na ² O.	K ² O.	H ² O.
55.12	0.65	8.20	0.33	0.75	31.18	1.66	1.01	2.21 = 100.90

(A. R. Leeds, *Sill. Am. J.* vi. 22).

ANTHRACENE, C¹⁴H¹⁰. The formation of this hydrocarbon from benzyl-toluene, C⁶H⁵—CH²—C⁶H⁴—CH³, shows, as already observed (2nd Suppl. 82), that it cannot have the constitution $\begin{array}{c} \text{C}^6\text{H}^5-\text{CH} \\ | \\ \text{C}^6\text{H}^4-\text{CH} \end{array}$ originally assigned to it by Graebe, which indeed belongs to the isomeric body phenanthrene (*ibid.* 84), but that it must be represented by the formula C⁶H⁵— $\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{array}$ —C⁶H⁴, its formation from benzyl-toluene being, in

fact, easily explained by aid of this formula, if we suppose that this latter hydrocarbon belongs to the ortho-series (1 : 2). On the other hand, the relations between benzyl-toluene and tolyl-phenyl ketone (2nd Suppl. 939), as hitherto understood, seem to show that benzyl-toluene belongs rather to the para-series. For, according to Kollaritz a. Merz, solid tolyl-phenyl ketone, heated with soda-lime, is resolved into benzene and paratoluic acid, whence it must be a para-compound; and this same ketone yields by oxidation a benzoyl-benzoic acid identical with that which is obtained by oxidation of Zincke's benzyl-toluene (*ibid.* 183), whence it would appear that this benzoyl-benzoic acid, and the benzyl-toluene from which it is formed, are also para-compounds. This apparent contradiction is however removed by the observation of Plascuda a. Zincke (*Deut. Chem. Ges. Ber.* vi. 906), that Zincke's benzyl-toluene is a mixture of two isomeric compounds, inasmuch as it yields by oxidation a mixture of parabenzoyl-benzoic acid with an isomeric acid (β -benzoyl-benzoic acid).

Further Bohr a. van. Dorp have shown (*Deut. Chem. Ges. Ber.* vii. 17) that liquid tolyl-phenyl ketone oxidised with potassium dichromate and sulphuric acid yields β -benzoyl-benzoic acid as well as the para-acid, and that this same ketone, when oxidised with manganese dioxide and sulphuric acid, yields anthraquinone (and probably anthracene as intermediate product), together with parabenzoyl-benzoic acid. This reaction indicates a relation between anthracene and β -benzyl-toluene.

Solid tolyl-phenyl ketone, on the other hand, oxidised with potassium dichromate and sulphuric acid, yields parabenzoyl-benzoic acid; with manganese dioxide and sulphuric acid it yields a large quantity of parabenzoyl-benzoic acid and a small quantity of β -benzoyl-benzoic acid, but not a trace of anthraquinone.

The liquid ketone heated with zinc-dust yields benzoyl-toluene, which however is immediately converted, by elimination of hydrogen and condensation, into anthracene; but when the solid ketone is similarly treated, this condensation does not take place, the product being pure benzyl-toluene, which remains unaltered when passed through a red-hot tube filled with pumice, whereas the mixture of the two benzyl-toluenes obtained by Zincke's process yields a large quantity of anthracene.

The relations between the several compounds above mentioned may be further shown by the following table:—

β (probably ortho-) benzyl-toluene.
Benzoyl-benzoic acid, m. p. 86°.
Liquid tolyl-phenyl ketone.
Anthracene.
Anthraquinone.

Parabenzyl-toluene.
Benzoyl-benzoic acid, m. p. 194°.
Tolyl-phenyl ketone, m. p. 67°.

That anthracene is not a para-derivative of benzene is shown by the following reactions: (1) Parabenzyl-toluene heated to redness does not yield anthracene. (2) Parabenzyl-toluene oxidised with manganese dioxide and sulphuric acid does not yield anthraquinone. (3) Parabenzyl-toluene passed over lead oxide or zinc-dust is not converted into anthraquinone or anthracene, whereas β -benzyl-toluene similarly treated does yield these derivatives.

Anthracene may therefore be represented by the formula C⁶H⁵— $\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{array}$ —C⁶H⁴, in

which the two CH-groups occupy the ortho-positions with respect to the groups C⁶H⁵ (see diagram, p. 96); and the assumption formerly made that benzyl-toluene is a 1 : 2 derivative of benzene (2nd Suppl. 82) may now be understood as applying to the

β -modification of that hydrocarbon, which belongs to the same series as liquid tolyl-phenyl-ketone (Behr a. van Dorp, *Deut. Chem. Ges. Ber.* vii. 16).

Preparation.—In preparing anthracene from tar, instead of stopping the distillation at the point where pitch remains in the retort, it is better, according to Versmann (*Diagl. pol. J. cevii.* 72), to push the operation to the end, so that nothing remains but a dense coke. The yield of anthracene is then 2 per cent., instead of only $\frac{1}{2}$ per cent. of the tar. The dead oil is separated from the distillate by strong pressure, and the pulverised residue is washed with petroleum spirit (b. p. 70° – 90°), and again pressed.

Estimation.—The most exact method of estimating the proportion of pure anthracene in the crude commercial article is to convert it into anthraquinone. This method presents the following advantages: (1) Anthracene dissolved in glacial acetic acid and boiled with chromic anhydride yields the theoretical quantity of anthraquinone. (2) This quinone is not further oxidised by long-continued treatment with the chromic solution; and (3) All other substances usually associated with anthracene in the commercial article, even chrysene and paraffin, are changed by the long-continued action of chromic anhydride into compounds which are soluble in alkaline solutions, and can thus be separated from the anthraquinone.

A gram of the anthracene to be examined is dissolved in 45 c.c. of boiling glacial acetic acid, filtered if necessary, and then a solution of 10 grams of chromic anhydride in 5 c.c. glacial acid and 5 c.c. water is gradually added, until a slight excess of chromic acid remains, even after long boiling; this may be readily ascertained by the red spot of silver chromate which will be produced on the surface of metallic silver by a drop of the liquid. It is then left to cool, diluted with 150 c.c. water, and, after being allowed to stand for some time, the quinone is collected on a filter and washed, first with water, then with a very dilute alkaline solution, and finally with water; 0.010 gram must be added to the weight of the quinone dried at 100° , being the loss occasioned by its solution in the dilute acid (E. Luck., *Deut. Chem. Ges. Ber.* vi. 1347). See also Paul a. Cownley (*Chem. News*, xxviii. 176); R. Lucas (*ibid.* xxx. 190; *Nicol. Zeitschr. Annal. Chem.* xix. 318; *Chem. Soc. J.* 1876, ii. 653; J. T. Brown, *Chem. News*, xxiv. 136; *Chem. Soc. J.* 1877, i. 233; Versmann, *Chem. News*, xxiv. 171, 191, 201; *Chem. Soc. J.* 1877, i. 347).

Fluorescence of Anthracene.—When anthracene in either of its forms—e.g. the olive-green commercial variety, the light-brown variety, the snow-like powder, or the pearly scales obtained by repeated crystallisation—is illuminated by a beam of sunlight which is condensed by a lens, and also passes through a cell containing a solution of ammonio-cupric sulphate, a fluorescent light is emitted, which when examined by a spectroscope, gives a spectrum consisting of four bright bands separated by darker intervals. The first bright band is situated in the red, the second in the yellow, and the two others in the greens. Absolutely pure anthracene, however, when examined as above, exhibits a blue fluorescence, and gives a perfectly continuous spectrum. Hence it is probable that the bright band spectrum is due to the presence of chrysogen in the ordinary samples of anthracene (*1st Suppl.* 459). Anthracene containing chrysogen also gives a very characteristic absorption-spectrum, showing two strongly-marked bands, one at F, the other towards G, and a less defined one at G, with a total extinction of all rays at a point slightly beyond G.

If a sample of ordinary commercial anthracene be dissolved in benzene, its solution shows a brilliant green fluorescence, which, on examination with the spectroscope, gives a spectrum of the same character as the solid, with the exception that all the bands are shifted towards the violet end of the spectrum (H. Morton, *Chem. News*, xvi. 199).

Reactions with Chlorine and Iodine.—When anthracene was digested for some days with antimony pentachloride, a current of chlorine being at the same time passed into the mixture, the greater part of the anthracene was carbonised, but on subjecting the product to distillation it was found to yield a crystalline sublimate. A portion of this sublimate dissolved in hot benzene, from which it separated in crystalline crusts which melted at 236° , 244° , and 252° after one, two, and three crystallisations. That portion of the sublimate which was insoluble in benzene yielded, on sublimation, beautiful needles, which melted above 330° , and contained an amount of chlorine nearly agreeing with that required by the formula, $C^{14}Cl^{12}H^4$. It is, however, probable that this substance is either derived from some impurity in the anthracene employed, or from a hydrocarbon formed by the polymerisation of anthracene, and that the true hexachloranthracene is to be found in the portion soluble in benzene.

When anthracene is fused with iodine, hydriodic acid is evolved, even if the temperature does not rise above 165° , and the greater part of the anthracene is carbonised; but a small portion of matter soluble in benzene or acetic acid is produced. When a so-

lution of iodine in phenol is boiled with anthracene, hydriodic acid is evolved. More definite results might perhaps be obtained by moderating the violence of the reactions, and assisting the action of the iodine by an oxidising agent (Bolas, *Chem. News*, xxviii. 167).

Action of Chlorochromic Acid.—This compound, added to a solution of anthracene in glacial acetic acid, oxidises it to anthraquinone, which, when precipitated with water, washed, dried, and subsequently sublimed or crystallised from alcohol, is obtained in splendid needles (Haller, *Compt. rend.* lxxiv. 558).

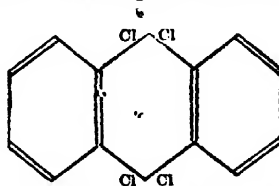
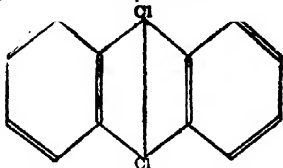
Action of Nitric Acid.—According to E. Schmidt (*Deut. Chem. Ges. Ber.* vii. 200), the mono- and dinitroanthracene described by Bolley (2nd *Suppl.* 83) as produced by the action of nitric acid on anthracene have no existence. The supposed mononitro-compound is in reality a compound of dinitro-anthraquinone and chrysene, and is produced only with certain varieties of commercial anthracene, those namely which contain hydrocarbons of higher order. Perfectly pure anthracene, when treated with nitric acid, does not yield a trace of any nitrated anthracene, but only the well-known oxidation-products, anthraquinone and dinitro-anthraquinone. The statement of Phipson (*Compt. rend.* lxxvi. 574) that nitro-anthracene is formed by treating anthracene with strong nitric acid, is also very doubtful, inasmuch as he merely obtained a viscid mass which he did not attempt to purify, but treated at once with tin and hydrochloric acid, whereby he obtained a basic compound, the so-called anthracenamine (2nd *Suppl.* 81). Schmidt, on repeating the experiment, found that the composition of the basic products thus obtained by no means agreed with the formula $C^{14}H^9.NH_2$, and moreover varied considerably in different preparations. It may therefore be concluded that no definite nitro-anthracenes have yet been obtained.

Halogen-derivatives (F. Schwarzer, *Deut. Chem. Ges. Ber.* x. 376). Dichloranthracene tetrabromide, $C^{14}H^6Cl^2.Br^4$, first obtained, but not examined by Graebe & Liebermann, is formed by exposing dichloranthracene for a considerable time to the action of bromine-vapour. It is slightly soluble in alcohol and ether, freely in chloroform and benzene, and crystallises in white silky needles melting at 186° . Heated to 180° – 190° , it is converted into dichloromonobromanthracene, $C^{14}H^7Cl^2Br$, which crystallises in small greenish-yellow laminae melting at 168° , easily soluble in chloroform. The tetrabromide boiled with alcoholic potash gives up 2HBr, and is converted into dichlorodibromanthracene, $C^{14}H^6Cl^2Br^2$, which is sparingly soluble in alcohol and glacial acetic acid, easily in benzene, and crystallises from the latter in small yellow needles melting at 251° – 262° . These two chlorobromoderivatives, when boiled with nitric acid, react like tetrabromanthracene (1st *Suppl.* 178), yielding respectively mono- and di-bromanthraquinone, but the oxidation is much slower than in the case of tetrabromanthracene, on account of the more intimate combination of the chlorine.

Dichloranthracene dichloride, $C^{14}H^6Cl^2.Cl^2$, is readily formed by passing chlorine into a solution of anthracene in chloroform. It crystallises in transparent prisms, melting at 149° – 150° , dissolves freely in benzene and chloroform, but only sparingly in alcohol and ether. When heated to 170° it yields trichloranthracene, together with a small quantity of dichloranthracene; the same decomposition takes place at the common temperature, even if the compound be kept in an atmosphere of hydrochloric acid. Trichloranthracene, $C^{14}H^7Cl^3$, crystallises from alcohol in long yellow needles melting at 162° – 163° .

The dichloride, $C^{14}H^6Cl^2.Cl^2$, heated with water or with alcoholic potash, is converted into anthraquinone; and the same reaction is produced by strong sulphuric acid at ordinary temperatures: $C^{14}H^6Cl^2.Cl^2 + 2H^2O = 4HCl + C^{14}H^8O^2$.

The reactions of dichloranthracene dichloride are most clearly explained by the following constitutional formula, which represents this compound as the chloride analogous to anthraquinone:



Dichloranthracene dichloride.

Methyl-anthracene. $C^{14}H^{12} = C^{14}H^9(CH_3)$, is formed by passing dimethylphenyl-methane, $CH_3(C^6H_4.CH_3)$, through a red-hot tube filled with fragments of porcelain, the change consisting in the loss of 4 atoms of hydrogen (Waller, *Deut. Chem. Ges. Ber.* vii. 1181).

Methyl-anthracene is also formed in considerable quantity when dimethyl-phenylethane, $\text{CH}_3\text{CH}(\text{C}^6\text{H}_5)\text{CH}_3$, is passed through a red-hot tube (O. Fischer, *ibid.* 1191). It is sparingly soluble in alcohol, ether, and acetic acid, and crystallises in glistening, yellowish, or white plates, melting at 198° – 201° , and dissolving readily in chloroform, benzene, and carbon sulphide. It sublimes in large white plates, exhibiting a fine blue fluorescence, and forms a picric acid compound closely resembling anthracene-picric acid. Chromic acid oxidises it to anthraquinone-carbonic acid, $\text{C}^{15}\text{H}^{10}\text{O}_4$, which sublimes in yellow needles melting at 282° . Methyl-anthracene, heated to 100° with strong nitric acid and alcohol, is oxidised to methyl-anthraquinone, $\text{C}^{15}\text{H}^{10}\text{O}_2$, which separates as a yellow precipitate (Fischer, *ibid.* viii. 675).

Dibromomethyl-anthracene, $\text{C}^{15}\text{H}^{11}\text{Br}_2$, is easily formed by adding bromine to a solution of the hydrocarbon in carbon sulphide. It forms yellow needles melting at 156° (Fischer).

Dibromodimethyl-anthracene, $\text{C}^{16}\text{H}^{12}\text{Br}_2$, is prepared by mixing the solutions of bromine and dimethyl-anthracene (2nd Suppl. 84) in carbon sulphide, and remains on evaporation as a yellow crystalline mass, easily soluble in benzene, ether, and absolute alcohol. When crystallised from glacial acetic acid, it forms yellow needles melting at 154° . It is decomposed by red-hot lime, with formation of dimethyl-anthracene.

Oryanthracene. See ANTHROL.

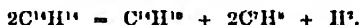
Isomerides of Anthracene.

1. Phenanthrene. The formula $\begin{array}{c} \text{C}^6\text{H}^4-\text{CH} \\ | \quad | \\ \text{C}^6\text{H}^4-\text{CH} \end{array}$, assigned to this hydrocarbon by Graebe and by Fittig (2nd Suppl. 84), represents it as diphenyl having two of its hydrogen-atoms replaced by acetylene; and this radicle may actually be introduced into the diphenyl-molecule by passing the mixed vapours of diphenyl and ethylene through a strongly ignited porcelain tube:



Benzene, styrolene, naphthalene, and a solid mixture of anthracene and phenanthrene are formed at the same time. A mixture of the last two hydrocarbons is also produced by the action of ethylene or styrolene on benzene (Barbier, *Compt. rend.* lxxix. 121).

Phenanthrene is also formed in small quantity, together with anthracene and toluene, when vapour of ditelyl or of benzyl-toluene is passed through a red-hot tube (Barbier):



Phenanthrene Hydrides.—Graebe prepared the tetrahydride, $\text{C}^{14}\text{H}^{14}$, by heating phenanthrene with hydriodic acid and phosphorus to 200° . According to Barbier, a heat of 280° is required to effect the combination, and the product, which is a liquid boiling at 260° – 270° , separates on cooling into a fluid and a solid portion. The liquid was treated with cold fuming nitric acid to remove benzene hydrocarbons and their derivatives; the greater part however remained unattacked even after prolonged treatment. Hydrochloric acid and tin were then added to remove nitro-compounds, and the product was dried. It then formed an oily liquid smelling like petroleum, boiling at 250° , and yielding by analysis 84.3 per cent. carbon and 15.2 hydrogen, agreeing very nearly with the formula $\text{C}^{14}\text{H}^{14}$, which requires 84.8 C. and 15.2 H. Hence Barbier infers that the liquid hydride, $\text{C}^{14}\text{H}^{14}$, which Graebe obtained was most probably a mixture of the saturated hydrocarbon, $\text{C}^{14}\text{H}^{14}$, with phenanthrene and intermediate hydrides; and that the so-called hydrides of toluene and xylene are probably similar mixtures. The solid (impure) hydride obtained by Graebe's process, on being heated in a sealed tube for five minutes, yielded diphenyl and benzene, the latter probably formed by the action of heat on the acetylene produced in the first instance:



A small quantity of phenanthrene is formed at the same time (Barbier).

2. Another isomeride of anthracene is obtained, together with anthracene and toluene, and an oily hydrocarbon, C^8H^{12} , by distillation of the secondary products formed in the preparation of benzyl-toluene. The oily hydrocarbon, when passed through a red-hot tube, yields a further quantity of anthracene and its isomeride. This iso-anthracene is moderately soluble in the usual solvents, crystallises in yellowish leaflets melting at 133° – 134.6° (phenanthrene melts at about 100°), and not easily sublimed. It may be oxidised to a quinone, $\text{C}^{14}\text{H}^6\text{O}_2$, which crystallises in long white needles melting at 211° – 212° , forms a blue mass with potash, and dissolves in

sulphuric acid more easily than anthraquinone (Weber a. Zinke, *Deut. Chem. Ges. Ber.* vii. 1153).

ANTHRACENE BLUE. This name is given to a blue colouring matter obtained in small quantity in the manufacture of alizarin. It is soluble in water, and dyes silk, wool, and cotton of a splendid and permanent blue (F. Springmühl, *Chem. Centr.* 1872, 728).

ANTHRACENE-CARBONIC ACID, $C^{14}H^{10}O^2 = C^{14}H^9.COOH$. Two acids of this composition are known, which may be distinguished as α and β .

The α -acid was obtained by Graebe a. Liebermann, by heating anthracene to 200° with liquid carbonyl chloride, digesting the product with sodium carbonate, and treating the filtered solution with excess of hydrochloric acid. It separates from alcoholic solution by spontaneous evaporation in long needles, melts at 206° , and is at the same time resolved into anthracene and carbon dioxide (1st *Suppl.* 179).

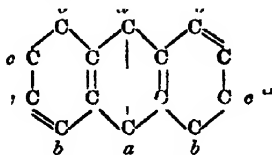
β -Anthracene-carbonic acid, discovered by Liebermann a. vom Rath (*Deut. Chem. Ges. Ber.* viii. 246), is produced by distilling the potassium salt of anthracene-sulphonic acid with perfectly dehydrated potassium ferrocyanide, boiling the distillate, which consists of unaltered anthracene and a nitril, with alcoholic potash as long as ammonia is evolved, and decomposing the filtered liquid with hydrochloric acid. The β -acid is then precipitated in yellow flocks, which may be purified by digestion with barium carbonate, whereby the easily soluble salt of anthracene-carbonic acid is obtained, while an insoluble salt, probably the anthracene-dicarbonate, remains behind; the solution treated with hydrochloric acid yields the β -acid.

β -Anthracene-carbonic acid is insoluble in water, slightly soluble in benzene, more easily in alcohol and glacial acetic acid, and separates on cooling from a hot saturated alcoholic solution in yellow needles; by more rapid concentration as a nearly amorphous mass. It dissolves also in dilute ammonia, and is precipitated therefrom by acids. It decomposes carbonates, and forms for the most part easily soluble salts. The barium and calcium salts are readily soluble and dry up to amorphous masses. The lead salt is a precipitate. The barium salt is not decomposed by carbon dioxide, but the ammonium salt loses all its ammonia on evaporation. The solution of its salts shows a greenish or blue fluorescence. But even if the colour of the solution be pure blue, the acid precipitated from it is always yellow.

The β -acid softens at 220° – 230° , melts irregularly at 260° , and when heated above 280° sublimes without decomposition in orange-yellow needles, which melt in the same manner as the unsublimed acid. These characters distinguish it from the α -acid, and a further distinction between the two is afforded by their behaviour with oxidising agents, the α -acid heated with a solution of chromic acid in glacial acetic acid being converted into anthraquinone, with evolution of carbon dioxide, whereas the β -acid is converted into anthraquinone-carbonic acid, which undergoes further decomposition only when the oxidising agent is in excess:



The structural formula of anthracene:



indicates the possible existence of three anthracene-carbonic acids, according as the group CO^2H is attached to the nucleus at one of the points a , b , or c . In Graebe a. Liebermann's acid (α), the carbonyl-group is most probably attached at one of the points a ; an acid so constituted must in fact give off carbon dioxide when oxidised, because the oxygen-atoms which convert it into a quinone will attach themselves to the points a . If, on the other hand, the carbonyl-group is attached at b or c , the quinonic oxygen-atoms may attach themselves at a without displacement of CO^2 . This therefore is probably the constitution of the β -anthracene-carbonic acid obtained by Liebermann a. vom Rath.

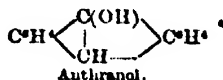
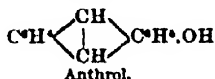
ANTHRACENE-SULPHONIC ACID, $C^{14}H^9SO^2H$ (E. Links, *J. pr. Chem.* [2], xi. 222). Two acids of this composition, α and β , are produced by heating 1 pt. of anthracene with 3 pts. of strong sulphuric acid in a water-bath, with constant stirring, till the greater part of the anthracene is dissolved, which may be known by

is forming a light brown solution on addition of water. Sulphurous anhydride is evolved during the solution of the anthracene, and if the action is allowed to go on too far, brown tarry products are formed. The product is purified by neutralising with lead carbonate, removing the lead with hydrogen sulphide, again neutralising with lead carbonate, and evaporating to the crystallising point. The β -lead salt then separates in prisms which may be purified by crystallisation, and on further concentration the α -salt separates in warty masses. The α -salt is produced in much larger quantity than the β -salt.

α -Anthracenesulphonic Acid, $C^{14}H^9SO^3H$, prepared from the lead or barium salt by precipitation with sulphuric acid, crystallises in yellow prisms or tables. The α -lead salt, $(C^{14}H^9SO^3)^2Pb + 4H^2O$, crystallises in light yellow scales, dissolves easily in hot water, but is less soluble in cold water. The α -barium salt, $(C^{14}H^9SO^3)^2Ba + 6H^2O$, crystallises in yellow needles, and is much more soluble in water than the β -salt. The sodium salt crystallises in microscopic scales.

β -Anthracenesulphonic Acid, $C^{14}H^9SO^3H$, crystallises in long well-developed prisms, difficultly soluble in water, and permanent in the air. The lead salt, $(C^{14}H^9SO^3)^2Pb + 7H^2O$, crystallises in yellowish prisms, and is very sparingly soluble in either hot or cold water. The barium salt is more soluble than the lead salt, and crystallises in nacreous plates, containing $7H^2O$. The sodium salt is sparingly soluble in water.

ANTHRAPHENOLS, $C^{14}H^{10}O = C^{14}H^9OH$. Of these bodies there are two metameric modifications, viz. :—

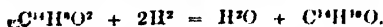


1. Anthrol is formed in two isomeric modifications by fusing the alkali-salts of α and β -anthracenesulphonic acid with caustic potash or soda in a silver basin, till a small quantity taken out and dissolved in water gives a copious precipitate on addition of an acid. The crude α -anthrol is a brownish-black mass; the β -modification is dark green. The crude products are purified by dissolving them in ether, which separates some tarry matter, filtering, and evaporating to dryness in an atmosphere of carbonic anhydride. As both the anthrols are very freely soluble in alcohol and ether, the crystals deposited from these solvents are but indistinctly formed, but good crystals may be obtained by precipitating an alcoholic solution with water. During all the operations the air of the apparatus should be replaced by carbonic anhydride.

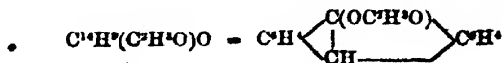
α -Anthrol crystallises in brilliant yellow needles, easily soluble in alcohol, ether, and benzene, not so easily soluble in chloroform, insoluble in water. On boiling with aqueous potash, it is oxidised to a dark brown body. It decomposes without fusion at 250° . Substitution-products are formed by bromine and sulphuric acid.

β -Anthrol crystallises in yellow prisms; it is less soluble in alcohol and ether than its isomeride. It oxidises to a green body on exposure to the air (Linke, *J. pr. Chem.* [2], xi. 227).

2. Anthranol.—This body, intermediate between anthraquinone and anthracene dihydride, $C^{14}H^{12}$, is obtained when anthraquinone (26 pts.) is heated with hydriodic acid of sp. gr. 1.7 (80 pts.) and phosphorus (4 pts.) in a vessel with reversed condenser for about an hour; if the action is allowed to go on further, anthracene dihydride is produced. The formation of anthranol is represented by the equation :

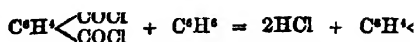


Anthranol crystallises in yellowish needles, melts at 163° – 170° , and at higher temperatures turns green and carbonises without volatilising. It is nearly insoluble in cold, more soluble in hot alkalis. The solution absorbs oxygen from the air and then on boiling deposits anthraquinone. Anthranol is also converted into anthraquinone by oxidation with nitric or chromic acid. By heating with zinc-dust it is reduced to anthracene. With acetic anhydride it forms a monoacetyl compound—



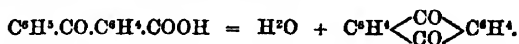
which crystallises in light yellow needles, melting at 126° – 131° (Liebmann & Topf, *Deut. Chem. Ges. Ber.* i. 1201).

ANTHRAQUINONE, $C^{14}H^8O^2$. *Formation*.—1. By the action of phthalic chloride on benzene :



When pure phthalic chloride was heated to 220° in sealed tubes with benzene and zinc-dust, a product was obtained which, after treatment with alcohol and sodium carbonate, yielded on sublimation yellow needles of anthraquinone. The yield was, however, very small, so that it is doubtful whether the above equation expresses the principal reaction (Piccard, *Deut. Chem. Ges. Ber.* vii. 1785).

2. From β -Benzoyl-benzoic Acid (Behr a. van Dorp, *ibid.* 578).—A mixture of 1 pt. β -benzoyl-benzoic acid and 2 pts. phosphoric anhydride with sand yields, when heated, a distillate of pure anthraquinone; but a better yield, amounting to 26 per cent. of the theoretical quantity, is obtained by heating the mixture to 200° for some hours, and then extracting the anthraquinone with benzene :



This reaction affords a strong confirmation of the views of Zincke and Fittig that anthraquinone should be regarded as a double ketone (*2nd Suppl.* 95). Parabenzoyl-benzoic acid does not yield anthraquinone.

Anthraquinone, in small quantity, is obtained by distilling benzoic acid with phosphoric anhydride. Here probably 2 mols. of benzoic acid coalesce, with elimination of water, to form β -benzoyl-benzoic acid, which then, by the further action of the dehydrating agent, yields anthraquinone. An analogous explanation may be given of the formation of anthraquinone by the distillation of calcium benzoate (Behr a. van Dorp). The formation of anthraquinone from benzoic acid may, on the other hand, be regarded as a simple dehydration thus, $2C^6H^5O^2 - H^2O = C^{14}H^8O^2$ (Kekulé a. Franchimont, *Deut. Chem. Ges. Ber.* v. 908).

On the preparation of Anthraquinone by the action of Chloride of Lime Solution and a metallic salt on Anthracene, see A. Henniges (*Dingl. pol. J.* cxxxi. 351; *Chem. Soc. J.* 1877, i. 360).

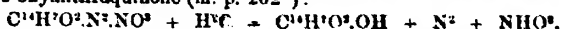
Nitro-anthraquinones and their Derivatives (Böttger a. Petersen, *J. pr. Chem.* [2], vi. 367; *Deut. Chem. Ges. Ber.* vi. 20). It was stated in the Second Supplement, on the authority of Böttger a. Petersen, that nitro-anthraquinones cannot be formed by the direct action of nitric acid on anthraquinone. Subsequent researches have, however, shown that the nitration of anthraquinone can be effected by the action of nitric acid alone without the aid of sulphuric acid, the product being mononitro-anthraquinone when anthraquinone is boiled with nitric acid of sp. gr. 1.5 for half an hour or longer, and dinitro-anthraquinone when it is boiled with red fuming nitric acid of sp. gr. 1.52 for several hours. Nitric acid of sp. gr. lower than 1.44 scarcely attacks anthraquinone dissolved in it, even on prolonged boiling.

Mononitro-anthraquinone, $C^{14}H^7(NO^2)O^2$.—To prepare this compound, anthraquinone is dissolved in six to twelve times its weight of warm nitric acid, of sp. gr. 1.5, and the solution is boiled for half an hour or longer. The liquid is then agitated with a large quantity of cold water, and the pale-yellow flocks thereby thrown down are washed with cold water. The product is a pale-yellow electric powder, subliming readily in delicate needles which melt at 230° . It is insoluble in water, very sparingly soluble in ether and alcohol, more freely in ethyl acetate, benzene, chloroform, turpentine, and glacial acetic acid, from which last it separates in fine crystals. It is easily soluble in nitrobenzene, in strong sulphuric acid, and in aniline (which is also an excellent solvent for anthraquinone and anthracene compounds generally), forming with the last a resinous compound, which dissolves with fine fuchsine-red colour in acetic acid, ethyl acetate, and other ethereal solvents. A mixture of strong nitric and sulphuric acids converts it into dinitro-anthraquinone. With fused alkalis it yields alizarin, together with a small quantity of anthraquinone.

Monoamido-anthraquinone, $C^{14}H^7(NH^2)O^2$.—This body is easily obtained by the action of reducing agents upon the preceding compound. It is best prepared by boiling mononitro-anthraquinone in fine powder with a moderately strong solution of sodium sulphhydrate for some time, diluting with water, cooling, filtering, and washing the product with cold water. Thus prepared, it forms a bright brick-red powder, which sublimes easily in small needles. Melting point 256° . It resembles the foregoing compound in solubility. It does not appear to combine with acids.

Diazo-anthraquinone nitrate, $C^{14}H^7N^2O^2.NO^2$.—A body having this composition is thrown down in the form of a pale red powder, when a current of nitrogen tetroxide

is passed into a solution of amido-anthraquinone in ether-alcohol. It is sparingly soluble in water, freely in ethyl acetate and alcohol, insoluble in ether. When warmed with water, it evolves nitrogen abundantly, and deposits flocks, which when heated yield a sublimate of glistening yellow crystals, exhibiting the properties of Graebe and Liebermann's oxyanthraquinone (m. p. 202°):



Mononitro-anthraquinone, heated to 200° with twelve times its weight of strong sulphuric acid, evolves a large quantity of sulphur dioxide. On afterwards pouring the solution into cold water, it deposits fine violet-red flocks of *imido-hydroxyl-anthra-*

quinone, $\text{HN}-\text{C}^{14}\text{H}^8\text{O}^2-\text{OH}$, which may be purified by washing with cold water and repeated evaporation of its alcoholic solution. It then forms a peach-blossom-coloured powder, melting when heated to a dark cherry-red liquid which yields a sublimate of slender rose-coloured needles melting at 240°. It is nearly insoluble in water, but dissolves more freely and with deep rose colour in alcohol, ether, ethyl acetate, chloroform, benzene, and glacial acetic acid, crystallising especially well from the last.

Dinitro-anthraquinone, $\text{C}^{14}\text{H}^6(\text{NO}^2)_2\text{O}^2$.—Of this compound there are two modifications, α and β . The former is produced by treating anthraquinone with a mixture of strong nitric and sulphuric acids, or, as above stated, with red fuming nitric acid at the boiling heat for several hours. Its properties and those of its reduction-derivatives have been already described (2nd Suppl. 91).

β -Dinitro-anthraquinone, identical with Anderson's dinitroxanthracene, and Fritzsche's oxydinitrophenone (1st Suppl. 180), is obtained, in combination with chrysene, by the action of dilute nitric acid on chrysene in alcoholic solution, and may be separated from the resulting compound, $\text{C}^{14}\text{H}^6(\text{NO}^2)_2\text{O}^2\cdot\text{C}^{18}\text{H}^{12}$, by the action of hot strong sulphuric acid (see CHRYSENE). It is very slightly soluble in alcohol, ether, carbon sulphide, chloroform, and benzene, and crystallises from boiling glacial acetic acid in brilliant yellow needles melting at 280°. When heated it sublimes with slight decomposition in almost colourless saturated plates. In warm sulphuric acid it dissolves without change, but on heating the solution it turns red and brown, and at 200° gives off sulphur dioxide. On pouring the solution into water, brownish-red flakes separate out, dissolving in alcohol, ether and acetic acid with a crimson colour, in ammonia with a reddish-violet and in potash with a bluish-violet colour. The dry compound is a glistening, black, amorphous powder (E. Schmidt, *J. pr. Chem.* [2], ix. 241).

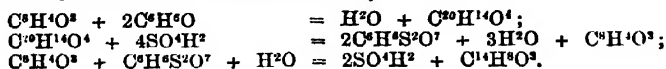
Oxyanthraquinones. Grimm, by heating hydroquinone with phthalic anhydride and strong sulphuric acid, obtained the phthalein of hydroquinone, together with quinzarin, an isomeride of alizarin. The other phenols, when heated with phthalic acid or anhydride, have hitherto been known to yield only phthaleins (2nd Suppl. 977); but the recent experiments of Baeyer & Caro (*Deut. Chem. Ges. Ber.* vii. 968) have shown that all the phenols, except resorcin and pyrogallol, when heated with phthalic acid, yield, according to the conditions of the reaction, either a phthalein by combination of 1 mol. phthalic anhydride with 2 mols. of the phenol, or an oxyanthraquinone by combination of 1 mol. phthalic anhydride with 1 mol. of the phenol. The reactions take place with or without the assistance of a dehydrating agent. At a moderate heat and with a moderate proportion of the dehydrant, phthaleins are formed, at higher temperatures, and with a larger proportion of the dehydrant, the product is an oxyanthraquinone. Resorcin and pyrogallol, even without the aid of sulphuric acid, always yield phthaleins; phenol, hydroquinone, and pyrocatechin, on the other hand, do not act upon phthalic acid without the aid of sulphuric acid, but with the assistance of that acid they produce phthaleins or oxyanthraquinones according to the circumstances above mentioned.

1. **MONOXYANTHRAQUINONE**, $\text{C}^{14}\text{H}^8\text{O}^2$.—Of this compound there are two modifications, distinguished by the names *oxyanthraquinone* and *erythroxyanthraquinone*, both produced by the action of phthalic anhydride on phenol in presence of sulphuric acid:



When the mixture of these substances is gently warmed, it gradually assumes a brownish-yellow colour, from formation of *phenol-phthalein*. On adding more sulphuric acid, phenolphthalein-sulphonic acid is produced, and if the heating be continued, and the temperature raised, the colour changes finally to a brownish-yellow. The addition of water at this stage causes the precipitation of yellow or brownish flocculi, consisting of a mixture of the two oxyanthraquinones. The formation of the phthalein does not appear to be essential to the production of oxyanthraquinone, since if phenol

be added to a sufficiently hot mixture of phthalic acid with sulphuric acid, the anthraquinone is obtained without coloration due to the phthalein being observed; and as phenolsulphonic acid, phenol-disulphonic acid, and oxysulphobenzide give a similar result, there is reason to suppose that the phenol-phthalein is converted by heating into phthalic acid and a sulpho-oxid of phenol, which substances, at a higher temperature, gradually react to form oxyanthraquinone:—



Salicylic acid, anisol, and even anisic acid behave like phenol; with salicylic acid, particularly when small quantities are employed, the reaction takes place with greater regularity than with phenol.

The two oxyanthraquinones may be separated by taking advantage of the fact that when the former is boiled with water and barium carbonate, it forms a soluble barium derivative, whereas the latter is without action on the carbonate.

Oxyanthraquinone, the modification which Liebermann obtained by the action of melting potash on anthraquinone-monosulphonic acid, crystallises from hot alcoholic solution in yellow laminae or needles, and from glacial acetic acid in long silky needles. It does not melt at 285°, but sublimes at a higher temperature in lemon-yellow laminae. When heated with zinc-dust, it yields anthracene, and when warmed with fuming nitric acid, large quantities of phthalic acid.

Oxyanthraquinone is very soluble in water. It dissolves in alkalis, forming reddish-yellow solutions; also in lime and baryta-water. Its solution in hot strong baryta-water deposits red crystals, which, after drying at 130°, have the composition represented by the formula $(\text{C}^{12}\text{H}^8\text{O}^3)_2\text{Ba}$. It is insoluble in acidulated water. Its *acetyl derivative*, $\text{C}^{12}\text{H}^7(\text{C}^2\text{H}_3\text{O})_2\text{O}^2$, crystallises from alcohol in small yellowish matted needles (Liebermann, *Liebig's Annalen*, clxxxiii. 145).

Erythroxyanthraquinone crystallises from alcohol in groups of pomegranate-yellow needles, which are more soluble in hot than in cold alcohol. It melts at 173°–180°, but sublimes already at 150°, condensing in long reddish-yellow needles of the colour of alizarin; when sublimed it crystallises in very fine needles. It is almost insoluble in dilute ammonia, and only slightly soluble in concentrated ammonia. With baryta or lime-water it yields a dark-red, almost insoluble lake, which is decomposed by carbonic acid. The absorption-spectrum of a solution of erythroxyanthraquinone in concentrated sulphuric acid exhibits a narrow band in the green, which does not appear in that of the isomeric body. Both yield ordinary alizarin when fused with potassium hydrate; the erythroxyanthraquinone, however, is less readily acted upon (Baeyer u. Caro).

Dioxyanthraquinones, $\text{C}^{12}\text{H}^8\text{O}^4 = \text{C}^{12}\text{H}^8(\text{OH})^2\text{O}^4$. These compounds admit of numerous modifications, depending: 1. On the manner in which the carbon-atoms in the group C^2O^2 are connected with the two benzene-residues C^6H^4 .—2. On the relative positions of the two hydroxyl-groups, which may be situated either (a) in the same benzene-group, but in different positions (ortho-, meta-, para-) with regard to each other. (β). In different benzene-groups, and likewise in different positions with regard to each other.

The number of possible dioxyanthraquinones is therefore very considerable. Of these, however, only eight are at present known: their names are given in the following table, together with the melting points of their diacetyl-derivatives:—

	M. P. of $\text{C}^{12}\text{H}^6(\text{C}^2\text{H}_3\text{O})^2\text{O}^4$.
Alizarin	160°
Quinizarin	200°
Purpuroxanthin	184°
Anthraflavic acid	228°
Isoanthraflavic acid	175°–180°
Anthraflavone	not determined
Chrysazin	220°–230°
Frangulic acid	184°

I. Dioxyanthraquinones, $\text{C}^6\text{H}^4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{C}^6\text{H}^4(\text{OH})^2$.

Alizarin. *Formation from Pyrocatechin.*—When pyrocatechin is gently heated with phthalic anhydride and sulphuric acid, the corresponding phthalein is apparently produced; but if the temperature be raised to 140°, the colour changes from rose-red to brown, and after a time water precipitates a brownish-black mass. The residue

from the alcoholic extract of this mass yields alizarin on sublimation. Guaiacol behaves in a similar manner. Protocatechuic acid also yields traces of alizarin, but is in great part decomposed in other ways. Hydroquinone heated in like manner yields quinizarin.

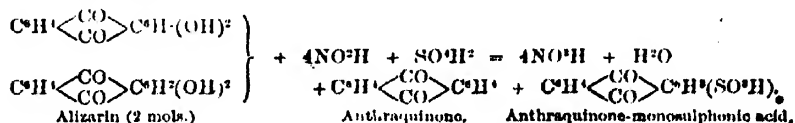
Preparation.—Liebemann a. Troschke (*Deut. Chem. Ges. Ber.* viii. 379) prepare pure alizarin by dissolving the commercial product in caustic soda, precipitating the sodium alizarate with carbonic acid, then decomposing it with an acid, and, after repeating these operations three times, boiling the partially purified alizarin with excess of baryta to remove monoxanthraquinone, and decomposing the barium compound of alizarin with an acid.

On the separation of Alizarin from Monoxanthraquinone, see also Willgerodt (*Dingl. pol. J.* ccxvii. 238; *Chem. Soc. Jour.* 1876, i. 249).

On the preparation of Artificial Alizarin, see also A. Ott (*Chem. News.* xxx. 113).

Melting Point.—According to Claus a. Willgerodt (*Deut. Chem. Ges. Ber.* viii. 530), perfectly pure alizarin melts at a temperature much higher than that usually assigned to it (215°), namely, at 289°–290°.

Reaction with Nitrous Acid.—When potassium nitrite is gradually added to a solution of artificial alizarin in strong sulphuric acid, or when nitrous vapours (from nitric acid and starch) are passed through the same solution, the original deep red colour of the liquid changes to brown, and a drop of the mixture added to caustic soda gives no longer the violet-red reaction of alizarin, but a yellow-red coloration. On further addition of the nitrite, the colour of the liquid ultimately becomes deep wine-yellow, a drop of it no longer gives any colour-reaction with soda, and on pouring it into water, a precipitate of anthraquinone is obtained, amounting to about a third of the alizarin employed. On mixing the yellow filtrate with calcium carbonate, precipitating the calcium with sodium carbonate, and evaporating the filtered liquid to dryness, an orange-yellow residue is left containing an anthraquinone-monosulphonic acid. The reaction may be represented by the following equations:



Precisely the same result is obtained with sublimed natural alizarin, showing that it is not due to the pre-existence of anthraquinone in the artificial alizarin. The reaction likewise goes on in the same way when glacial acetic acid instead of sulphuric acid is used to dissolve the alizarin.

The above-mentioned colour-reaction with sodium hydrate shows that the alizarin is first converted into monoxanthraquinone, and afterwards into anthraquinone.

Purpurin, natural or artificial, when similarly treated, gives the same final result, but does not appear to be first converted into alizarin, the deep red alkali reaction of purpurin quickly passing into wine-red, but not into violet. This agrees with the observation of Rosenstiehl, that purpurin is converted by reduction, not into alizarin, but into purpuroxanthin (Nienhaus, *Deut. Chem. Ges. Ber.* viii. 774).

On the function of Acids in Dyeing with Alizarin, see Rosenstiehl (*Compt. rend.* lxxxii. 86).

On Alizarin as an indicator in Volumetric Analysis, see ANALYSIS (p. 83).

Bromalizarin, $\text{C}^{14}\text{H}^7\text{BrO}^4$ (Perkin, *Chem. Soc. Jour.* [2], xii. 401).—This compound is prepared by heating about 3 parts of pure dry alizarin and 2½ parts bromine dissolved in carbon sulphide, to 180°–190° in sealed tubes for four or five hours, opening the tubes when the reaction is completed, to allow the excess of hydrogen bromide to escape, and transferring the contents to a shallow dish to allow the carbon sulphide and the remaining bromine to evaporate. The orange-coloured powder thus obtained may be purified by two or three crystallisations from glacial acetic acid.

Bromalizarin thus prepared crystallises in orange or brownish-orange-coloured needles, often grouped in small tufts. When heated slowly, it first melts to a brown liquid, which solidifies to a crystalline mass on cooling; but, if further heated, it gives off orange-coloured vapours, which when condensed form a sublimate of feathery groups of needles of a bright orange-red colour, consisting apparently of unchanged bromalizarin.

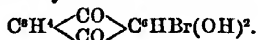
Bromalizarin dissolves with difficulty in alcohol, but more readily in glacial acetic

acid. It dissolves in a solution of potassium hydrate with a blue colour; in ammonia, and in sodium carbonate, with a purple colour. The coloured solutions produced by these reagents are exactly of the same tint as those given by alizarin. The solution in potassium hydrate also gives the same bands when viewed with the spectroscope.

As a dyeing agent, bromalizarin retains all the properties of combining with mordants possessed by alizarin, and the colours produced by it appear to be equally fast. The shade of colour produced is, however, not the same, the reds being less purple and the purples less blue than those produced with alizarin.

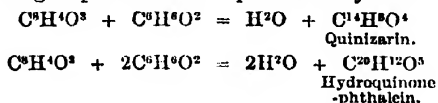
Bromalizarin heated to 100° with ammonia in a sealed tube is quickly converted into an indigo-blue nitrogenous product. It is rapidly attacked by nitric acid, the mixture when heated giving off abundance of red fumes and bromine-vapour, and yielding a solution containing oxalic and phthalic acids. From the formation of the latter acid, it may be inferred that the bromine in bromalizarin exists in the carbon-group which contains the two hydroxyls, as otherwise the product of the oxidation should be a bromophthalic acid.

The formula of bromalizarin may therefore be written :—



Dinitrophenyl-alizarin, $\text{C}^4\text{H}^4\text{O}^2 \begin{matrix} \text{OH} \\ \text{O.C}^6\text{H}_3(\text{NO}_2)_2 \end{matrix}$, is formed by treating alizarin with dinitrophenyl chloride (Claus a. Willgerodt, *Deut. Chem. Ges. Ber.* viii. 530°).

Quinizarin (F. Grimm, *Deut. Chem. Ges. Ber.* vi. 506). This body is produced, simultaneously with the phthalein of hydroquinone, by heating hydroquinone to 130°–140° with strong sulphuric acid and phthalic anhydride :



The quantities of the two compounds actually obtained are however much below those required by the preceding equations, viz., 26 to 25 per cent. of the theoretical amount of the phthalein, and only 1 to 2 per cent. of the quinizarin.

Quinizarin is likewise formed by the action of phthalic anhydride on all substances which, when heated with sulphuric acid, yield either hydroquinone or its sulpho-derivatives. Thus it is formed from quinic acid, which is converted into *a*-hydroquinone-disulphonic acid on heating with sulphuric acid; and from potassium thiochronate, which, when heated with sulphuric acid, furnishes *B*-hydroquinonedisulphonic acid.

Quinizarin crystallises from alcohol in red needles, from ether in yellow plates; it melts at 194°–195° (uncorrected) after sublimation; at 192°–193° after crystallisation from alcohol. It perhaps bears to munjistin the same relation as alizarin to purpurin. With alkalis it gives a blue solution with a slight violet tint; with baryta, a beautiful blue-violet compound; with alumina, a red lake with a violet shade; and with magnesia, a deep blue violet. The weak alkaline solution becomes brown-red on the addition of ferric chloride, and gives a dark red precipitate with lead acetate.

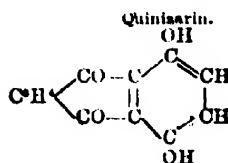
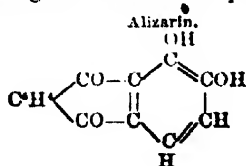
Quinizarin, in most of its properties, bears a strong resemblance to alizarin, and, like the latter, yields anthracene* (m. p. 210°–212°) when heated with zinc-dust. The chief differences between the two are that alizarin gives greenish-yellow fluorescent solutions, whereas quinizarin gives non-fluorescent solutions, and that the spectra of the two exhibit different absorption-bands. A comparative table of these spectra is given in Grimm's paper above referred to.

Constitution of Alizarin and Quinizarin.—These two dioxyanthraquinones, being formed by the action of phthalic anhydride and sulphuric acid on dioxybenzenes, the former from pyrocatechin, the latter from hydroquinone, must have their two hydroxyls in the same benzene-nucleus; that is to say, they must both be represented by the formula :

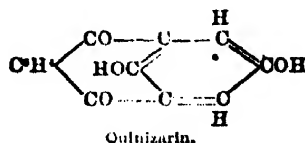
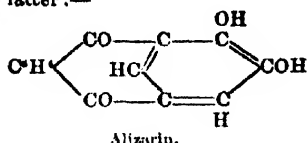


Moreover, they must have their hydroxyls in the same relative positions as in the phenols from which they are derived, which will therefore be, for alizarin 1 : 2, and for quinizarin 1 : 4. There still, however, remains a question as to the mode of attachment of the ketonic groups, CO, to the two benzene-nuclei. Now the formation of alizarin from phthalic acid, and its conversion into that acid by oxidation, afford sufficient proof that the two CO-groups are attached to contiguous carbon-atoms of

one of the benzene-nuclei. But with regard to their mode of attachment to the other benzene-group we cannot at present speak with equal certainty. It has indeed been shown by Behr a. van Dorp (p. 92) that anthracene (and therefore anthraquinone) is not a para-derivative of benzene; consequently, the two carbon-atoms in the second benzene-group to which the CO-groups are attached cannot be in the para-position with regard to each other; and this conclusion is confirmed by the formation of two isomeric monooxyanthraquinones (p. 100): for a para-derivative in which the two substituted radicles are identical cannot yield more than one tri-derivative (para-dibromobenzene, for example, yields only one mononitro-dibromo-benzene). But whether the two carbon-atoms in question are in the relative position 1 : 2 or 1 : 3 must for the present remain undecided, although the balance of evidence appears to be in favour of the 1 : 2 position (p. 92). In the former case the formulae to be assigned to alizarin and quinizarin are:—

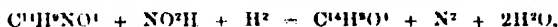


In the latter:—



(Baeyer a. Caro, *Deut. Chem. Ges. Ber.* vii. 968).

3. **Purpuroxanthin**, $C^{14}H^8O^2.C^{12}H^2(OH)^2$. This dioxanthraquinone was first obtained by Schützenberger from madder (2nd Suppl. 1027). It may be prepared artificially from purpurin by reduction with stannous chloride (Schützenberger) or with phosphorus. A hot alkaline solution of purpurin dissolves phosphorus without evolution of hydrogen, and the purpurin is quickly reduced to purpuroxanthin, which may easily be separated from the solution as a bright yellow crystalline powder (Rosenstiehl, *Compt. rend.* lxxix. 764). It is also formed by the action of nitrous acid on purpuramide (Liebermann a. Fischer, *Deut. Chem. Ges. Ber.* viii. 974):



Purpuroxanthin sublimes in needles of the same colour as alizarin; it dissolves in acetic acid, alcohol, and benzene, also in alkalis, forming solutions of a beautiful red colour, which is changed to brownish by reducing agents, but reappears on pouring the liquid into acidulated water (Rosenstiehl). According to Rosenstiehl, it does not dye with iron or alumina mordants; according to Schützenberger, on the contrary, it dyes pale grey with the former, orange-yellow with the latter, the colours being however less pure than those of purpurin.

Purpuroxanthin boiled with hydriodic acid and phosphorus is first reduced to a greenish-yellow body, $(C^{14}H^{10}O^2)$, or $(C^{14}H^{12}O^2)$, which dyes alumina mordants like quercitrin; but, by prolonging the action, anthracene is obtained, as is likewise the case when purpuroxanthin is treated with zinc-dust. When boiled in alkaline solution, purpuroxanthin is oxidised to purpurin, identical with that of madder, and with that which is formed by the oxidation of alizarin (Rosenstiehl).

The formation of purpuroxanthin by reduction of purpurin, and its reconversion into purpurin by oxidation, show that these two colouring matters are similarly constituted. Now Baeyer has lately shown that in purpurin the three hydroxyls are situated in the same benzene-nucleus: consequently, purpuroxanthin must, like alizarin and quinizarin, have its two hydroxyls in the same benzene-group; and this conclusion is confirmed by the observation that purpuroxanthin when oxidised with nitric acid is converted into phthalic acid, together with oxalic acid and a resinous substance (Liebermann a. Fischer). Moreover, since alizarin and quinizarin have their two hydroxyls in the ortho- and para-positions respectively, it follows that in purpuroxanthin the two hydroxyl-groups must be to one another in the meta-position 1 : 3.

Purpuroxanthin heated with aqueous ammonia is converted into an amide, from which it has not yet been found possible to eliminate the amidogen-group.

Diacetyl-purpuroxanthin, $C^{14}H^4(C^2H^3O^2)O^4$, crystallises in light yellow needles melting at 183° – 184° (Liebermann & Fischer).

Purpuroxanthic Acid, $C^{14}H^4O^6 = C^{14}H^4O^4.CO^2H$ (Schunck & Roemer, *Chem. Soc. Jour.* 1877, i. 666; *Deut. Chem. Ges. Ber.* x. 172).—This compound, related to purpuroxanthin in the same manner as oxybenzoic acid to phenol, is one of the constituents of madder, and may be extracted from commercial purpurin by treating that substance with boiling alum-liquor; adding hydrochloric acid to the solution; treating the resulting precipitate with boiling alcohol, which partly dissolves it, and the undissolved portion with boiling alcohol slightly acidulated with hydrochloric acid, whereupon it dissolves, forming a solution which deposits a small quantity of crystallised purpuroxanthic acid. An additional quantity was obtained from the mother-liquor, which remained after recrystallising the purpurin (partly purified, as above) from boiling alcohol. This mother-liquor, which also contained alizarin, purpurin, and a substance (not yet identified) soluble in boiling baryta-water, was evaporated to dryness, and the residue was treated with boiling water, in which purpuroxanthic acid dissolves more readily than the other substances. The filtered liquid mixed with hydrochloric acid gave an abundant orange-coloured precipitate, which was treated with boiling-water, to remove the purpuroxanthin and the unknown substance accompanying it, the barium purpuroxanthate remaining undissolved. This salt was decomposed with hydrochloric acid, and the liberated purpuroxanthic acid was crystallised from boiling alcohol, the accompanying traces of alizarin and purpurin remaining in the alcoholic mother-liquor. After two or three crystallisations from glacial acetic acid, it was obtained pure.

Purpuroxanthic acid possesses properties by which it may readily be distinguished from pseudopurpurin, purpuroxanthin, and the other colouring matters described by Schützenberger and Schiffert, as existing in crude purpurin (iv. 751). It melts at 231° , and splits up between 232° and 233° into purpuroxanthin and carbon dioxide, so that it can scarcely be sublimed without decomposition. It is more soluble in boiling water than most madder-colouring matters, and forms a yellow solution which deposits crystalline flocks on standing. It dissolves easily in hot spirits of wine, giving a yellow solution, which on cooling deposits yellow lustrous needles. These needles, on exposure to the air, gradually become dull, apparently from loss of water of crystallisation. Concentrated alcoholic solutions, however, frequently yield crystalline plates, which retain their lustre when heated, and are therefore probably anhydrous. Purpuroxanthic acid dissolves easily in glacial acetic acid on boiling, giving a yellow solution with a slight green fluorescence, which, on cooling, deposits yellow shining micaceous scales resembling iodide of lead. Dilute solutions deposit on standing long crystalline needles of a deep yellow or reddish-yellow colour. On one occasion flat triangular plates were obtained, which became completely opaque on drying.

Purpuroxanthic acid is soluble in ether, chloroform, and benzene. It dissolves in concentrated sulphuric acid, giving an intensely yellow solution, which shows no absorption-bands. It is easily decomposed by treatment with boiling nitric acid of ordinary strength. It dissolves in caustic potash, yielding a solution resembling in colour alkaline solutions of purpuroxanthin, but with a more decided red tinge; it shows no trace of absorption-bands. When treated for some time with boiling caustic potash-ley, purpuroxanthic acid yields purpurin, but whether purpuroxanthin is formed as an intermediate product has not been ascertained. It is quite insoluble in baryta- and lime-water. The ammoniacal solution gives red precipitates with the chlorides of barium and calcium. An alkaline solution gives with alum a precipitate which dissolves completely in an excess of boiling alum-liquor, yielding a yellow solution which is not fluorescent, and shows no absorption-bands; on standing it deposits orange-coloured flocks.

Purpuroxanthic acid dissolves in a boiling solution of ferric chloride, with deep reddish-brown colour, and is reprecipitated by hydrochloric acid in yellow flocks. The alcoholic solution gives with acetate of lead an orange-coloured precipitate, the supernatant liquid being colourless. Since purpuroxanthin is not precipitated from its alcoholic solution by acetate of lead, the two substances may by this means be distinguished as easily as by the difference in their barium compounds. Purpuroxanthic acid in the freshly precipitated state dyes alumina mordants an orange, and iron mordants a brown colour; but the colours are fugitive, and disappear entirely on treatment with boiling soap-liquor.

Purpuroxanthic acid is identical with the substance called ϵ -purpurin, which Rosenstiehl obtained by boiling pseudopurpurin with water (*Compt. Rend.* lxxxiii. 827). Rosenstiehl at first regarded this substance as an isomeride of purpurin, but

he has since recognised its identity with purpuroxanthic acid (*ibid.* lxxxiv. 659). Munjistin, the colouring matter obtained by Stenhouse from munjeet or East Indian madder (iii. 1061), is also most probably identical with purpuroxanthic acid. Its composition, as determined by Stenhouse, agrees indeed more nearly with the formula $C^{16}H^8O^8$ than with $C^{14}H^8O^8$; but its principal properties are exactly those of purpuroxanthic acid, as Schunck & Roemer find that it begins to soften at 225° , melts completely at 230° , is resolved at a higher temperature into carbon dioxide and purpuroxanthin, and is converted by fusion with caustic alkali into purpurin.

II. *Dioxyanthraquinones*, $C^8H^4(OH) \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C^8H^4(OH)$.

4 and 5. **Anthraflavic** and **Iso-anthraflavic Acids** (Schunck & Roemer, *Deuts. Chem. Ges. Ber.* viii. 1628; ix. 379; Perkin, *Chem. Soc. Jour.* 1876, i. 851). Anthraflavic acid, an isomeride of alizarin, was originally obtained as a byo-product in the preparation of the latter by melting anthraquinone-disulphonic acid with potash (2nd Suppl. 86).

Iso-anthraflavic acid was prepared by Schunck & Roemer, from a byo-product obtained in Perkin's alizarin works, by treating crude alizarin (prepared chiefly from anthraquinone-disulphonic acid) with lime-water, and precipitating the red extract with hydrochloric acid. This precipitate having been freed from a small quantity of anthraquinone by solution in dilute caustic soda-ley, the filtrate mixed with hydrochloric acid yielded a yellow gelatinous precipitate, partly soluble in cold baryta-water, and forming a blood-red solution from which acids threw down a yellow gelatinous precipitate of iso-anthraflavic acid. By repeated crystallisation from alcohol, this compound is obtained mostly in long yellow needles; sometimes, however, in laminae, which may be converted into the needles by further crystallisation.

The portion of the original precipitate which is soluble only in hot baryta-water consists of anthraflavic acid.

Perkin has obtained iso-anthraflavic acid directly from anthraquinone-disulphonic acid, by heating a salt of that acid with dilute potash-solution (containing 6 per cent. KHO). The mixture was placed in a strong mercury bottle, the plug being well luted and tightly screwed down, and then heated in an oil-bath to 180° - 190° for six or seven hours. In this way scarcely any anthrapurpurin was formed, the product being a red-brown solution. On treating this with acids, large quantities of sulphurous anhydride were given off, and a yellow precipitate was formed; this was collected on a filter and washed. On treating it with cold baryta-water it mostly dissolved. The solution when concentrated deposited a dark-coloured product, apparently crude barium anthraflavate, leaving a dark-red solution, which, when acidified, gave a greenish-yellow precipitate containing a large quantity of iso-anthraflavic acid, purifiable by repeated crystallisation from glacial acetic acid, in which it is slightly soluble.

The crystals of iso-anthraflavic acid contain several molecules of water, the last of which they do not give off till heated to 120° - 150° , at which temperature they also lose their lustre. Cold baryta- and lime-water dissolve iso-anthraflavic acid with dark-red colour. It does not possess tinctorial properties.

By fusion with potash, iso-anthraflavic acid is converted into anthrapurpurin, and anthraflavic acid into flavopurpurin* (p. 111).

Barium Iso-anthraflavate, $C^{16}H^4BaO^8$, is very soluble in water, and crystallises, though with some difficulty, in dark red shining needles, which decompose readily on exposure to the air, and give off their water of crystallisation at 150° .

Barium Anthraflavate is but very slightly soluble in cold water. It resembles the iso-anthraflavate in appearance, and is likewise decomposed, though less quickly, on exposure to the air. The crystals, when left over sulphuric acid, give off a large quantity of water, lose their lustre, and become lighter-coloured. The last two molecules of water are given off at 160° - 180° (Schunck & Roemer). According to Perkin, the salt dried at 180° has the composition $2C^{16}H^4BaO^8 + H^2O$.

The following table exhibits a comparative view of the properties of the two isomeric acids:—

* It would be better if the names of the two acids were transposed.

Iso-anthraflavic Acid.

Crystallises from aqueous alcohol with water of crystallisation.

Melts above 330°.

Less soluble in glacial acetic acid than in alcohol.

Nearly insoluble in benzene, chloroform, and ether.

Dissolves in hot concentrated sulphuric acid with deep red colour.

Easily soluble in cold baryta-water.

Easily soluble in lime-water.

From the aqueous solution of the barium salt, carbonic acid separates free iso-anthraflavic acid, but the salt is reproduced on boiling.

Soluble in alcoholic acetate of lead.

The solutions in alkalis and alkaline earths have a deep red colour.

Sublimes in shining yellow needles and laminae.

Does not colour mordants.

Anthraflavic Acid.

Crystallises without water.

The same.

The same.

The same.

Dissolves in strong sulphuric acid with yellow colour.

Insoluble in cold baryta-water.

Slightly soluble in cold, nearly insoluble in hot lime-water.

The same.

The same.

The solutions in alkalis and alkaline earths have a more or less yellowish-red colour.

The same.

The same.

Tetrabrom-isoanthraflavic Acid, $C^{14}H^4Br^4O^4$, is prepared by dropping bromine in large excess into an alcoholic solution of iso-anthraflavic acid. The liquid in a few minutes solidifies to a crystalline pulp of yellow needles slightly soluble in alcohol, somewhat more easily in glacial acetic acid, from which solvent it may be recrystallised for purification.

Tetrabromanthraflavic Acid, prepared in like manner, is nearly insoluble in both the solvents above mentioned. The crude product, which also crystallises in yellow needles, was freed from unattacked anthraflavic acid by repeated boiling with alcohol (Schunck a. Roemer).

Diacetyl-isoanthraflavic Acid, $C^{14}H^4(C^2H^3O)^2O^4$, is formed by heating the acid with acetic anhydride to 160°–180°. It dissolves with some difficulty in alcohol, more readily in glacial acetic acid, and separates from the former solvent in pale yellow microscopic crystals, which cake together at 175° and melt at about 195°. The acetyl is removed by heating with alcoholic potash, and the resulting liquid, treated with acid, yields a precipitate of iso-anthraflavic acid (Schunck a. Roemer).

Diacetylanthraflavic Acid, discovered by Perkin, is prepared in a similar manner (2nd Suppl. 87). It differs from the preceding acid by its greater facility of crystallisation, and by its melting point, 227° (Schunck a. Roemer), 228°–229° (Perkin).

Diethyl-isoanthraflavic Acid, $C^{14}H^4(C^2H^5)^2O^4$, is prepared by heating iso-anthraflavic acid, for a few hours, with soda-ley, ethyl iodide, and a small quantity of alcohol. The product is a body insoluble in caustic alkali, and purifiable by one crystallisation from alcohol, from which it separates, in long shining light-yellow needles. This compound is quite insoluble in water, slightly soluble in alcohol and ether, more freely in glacial acetic acid and benzene, soluble also with red-violet colour in strong sulphuric acid, the solution exhibiting two indistinct absorption-bands in the green and yellow, and, on stronger concentration, likewise an absorption-band in the blue. It melts at 193°–194° (Schunck a. Roemer).

Diethylanthraflavic Acid, prepared like the preceding compound, forms somewhat lighter-coloured crystals, and in most respects resembles the acid last described. Its solution in strong sulphuric acid is red, and gives an absorption-band at the border of the green and blue, much more distinct than that formed by anthraflavic acid under similar conditions.

Diethylanthraflavic acid melts at 232°, and solidifies, even when quickly cooled, in large prismatic crystals, a property likewise possessed by diethyl-isoanthraflavic acid.

Dimethylanthraflavic Acid, prepared in like manner with methyl iodide, resembles the diethyl-compound in most respects, but melts at 247°–248° (Schunck a. Roemer).

6. **Anthraflavone** (Barth & Senhofer, *Liebig's Annalen*, clxx, 100). This modification is produced in small quantity by dry distillation of oxybenzoic acid, and much more abundantly by heating that acid with slightly diluted sulphuric acid (9 of strong acid to 1 of water) to 180°–200° in sealed tubes, for three or four hours:



On pouring the contents of the tubes into water, a dark-green precipitate of the new compound is produced, whilst sulphybenzoic acid and the excess of sulphuric acid remain in solution. The green precipitate is dissolved in baryta-water, boiled with animal charcoal, and reprecipitated by hydrochloric acid; after being washed and dried, it is mixed with animal charcoal and exhausted with ether. To obtain the substance of a pure yellow colour it is necessary to repeat the latter operation several times. In this state it consists of yellow crystalline crusts composed of microscopic needles. It dissolves with difficulty in ether, more readily in alcohol, but is almost insoluble in water. It remains unchanged at 300°, and sublimes at a somewhat higher temperature without previous fusion. It dissolves in concentrated sulphuric acid, and is precipitated unchanged on the addition of water. Alkalis dissolve it with a deep brownish-red colour.

Anthraflavone, like its isomerides, is reduced to anthracene by the action of heated zinc-dust. The mode of its formation indicates that its two hydroxyle are situated in different benzene rings.

Anthraflavone acts like a bibasic acid, exchanging 2 atoms of hydrogen for metals, thus:



The **potassium salt** is prepared by dissolving anthraflavone in potassium carbonate, evaporating to dryness in a vacuum, and extracting with absolute alcohol, in which it is soluble. On evaporation, the compound is left in brown-red, crystalline masses consisting of microscopic needles. Dried at 200°, it has the formula $C^{14}H^4K^2O^4$. The **sodium salt**, like the potassium salt, forms reddish-brown microscopic needles.

The **barium salt** is obtained by dissolving the anthraflavone in ammonia, driving off the excess of ammonia at 100°, and precipitating the solution with barium chloride; or by dissolving the substance in barium hydrate, evaporating the solution in a vacuum, and removing the excess of barium hydrate by washing with cold water. The residue when dissolved in boiling water, filtered, and again evaporated in a vacuum, leaves the compound in brown-red needles of the formula $C^{14}H^4BaO^4 + 5H^2O$.

A **basic lead salt** of greyish-red colour is precipitated on adding an alcoholic solution of basic lead acetate to a solution of anthraflavone; and a reddish-brown, flocculent **silver salt** is precipitated from the ammonium compound by silver nitrate.

The action of fused **potassium hydrate** on anthraflavone produces a violet-blue colour which changes to reddish-brown; and by treatment with sulphuric acid and ether in the usual way, a product is obtained, soluble in water, and consisting principally of paraoxybenzoic acid, with a comparatively small amount of oxybenzoic acid.

A **nitro-compound** is produced by the action of boiling nitric acid on anthraflavone, but it has not yet been obtained in a state of purity; an **oxidised product** is also formed at the same time. Anthraflavone is not changed by the action of sodium amalgam.

Diacetyl-anthraflavone, $C^{16}H^6(C^2H^3O)^2O^4$, is formed when anthraflavone is heated in closed tubes to 120° with acetyl chloride, or by treating its potassium compound with the chloride. It crystallises from ether in pale-yellow crusts, but appears to be decomposed by alcohol.

According to Rosenzweig (*Deut. Chem. Ges. Ber.* ix, 946), crude anthraflavone is separable into two products, which behave differently towards bases:—

α-Anthraflavone.

The sodium-compound is very freely soluble in water, yielding a red solution.

β-Anthraflavone.

The sodium-compound is sparingly soluble, especially in excess of soda. It crystallises in brilliant red needles, the solution of which is inclined to yellow.

α-Anthraflavone.

Dissolves easily in baryta-water with red colour.

In alkaline solutions combines for the most part with alumina.

Is easily and completely converted into an isomeride of purpurin when heated to 130°–145° with potash in close vessels.

β-Anthraflavone.

Dissolves in baryta-water only when boiling. The compound separates in red needles on cooling.

Does not combine with alumina, but remains in solution.

Remains unaltered at 130°–135°, oxidation first commencing at 200°–205°. On this behaviour is based a method of purifying *α*-anthraflavone.

Identical with *β*-anthraflavone is, perhaps, a di-*α*-anthraquinone, described by Ullrich a. Perger (*ibid.* ix. 131 and 574), under the name of *Anthracanthic acid*, and said to be obtained, under peculiar circumstances only, as a bye-product in the manufacture of alizarin. It closely resembles *β*-anthraflavone, especially in being converted by oxidation in alkaline solution at 200° into an isomeride of purpurin exactly similar to that which Rosenstiehl has obtained from *β*-anthraflavone.

7. Chrysazin (Liebermann a. Giesel, *Deut. Chem. Ges., Ber.* viii. 1643; ix. 329), is produced by de-amidation of hydrochrysamme, $C^{14}H^{14}(NH^2)O^4$ (iii. 191). For this purpose, the sulphuric acid solution of hydrochrysamme, mixed with sufficient water to give it a pulpy consistence, is kept cool by snow, and nitrous acid vapour is passed into it till the pulp liquefies and assumes a cherry-red colour, and the nitrous vapours are no longer absorbed. The mass is then added, with stirring, to well-cooled absolute alcohol, and the brown-red precipitate of a diazo-compound thereby produced is quickly collected in a filter, heated to 60° with alcohol, till nitrogen and aldehyde begin to escape, then boiled for some time to complete the reaction. The solution is filtered to separate a nitrogenised substance insoluble in alcohol, and the alcoholic filtrate is mixed with water, which throws down the chrysazin in yellow-brown flocks.

For further purification chrysazin is dissolved in ether, and then recrystallised from alcohol or acetic acid, from either of which it separates in red-brown lustrous needles, from alcohol also in golden-yellow laminae, the two forms being easily and completely convertible one into the other. It melts at 191°; dissolves in alkalis with yellow-red colour, very slightly in alkaline carbonates and in ammonia, and forms red precipitates with baryta- and lime-water; does not dye mordanted cotton. By heating with zinc-dust it is reduced to anthracene.

Tetranitrochrysazin, $C^{14}H^{14}(NO^2)_4O^4$, formed by treating chrysazin with fuming nitric acid, is identical in every respect with chrysammic acid prepared from aloes. The compound obtained from either source separates from its solution in fuming nitric acid, after the excess of that acid has been blown away by a current of air, in small brightly specular monoclinic crystals with short prismatic development. Axial ratio $a : b : c = 1 : 0.90888 : 1.8363$. Angle of inclined axes = 74°. Combination $\infty P. \infty P\infty. R\infty$.

The metallic chrysammates or tetranitro-chryszakates are prepared by boiling the acid with the corresponding acetates, and crystallising the resulting precipitates. They exhibit the same characters whether prepared from chrysammic acid (from aloes) or from tetranitrochrysazin.

The **potassium salt**, $C^{14}H^{14}(NO^2)_4O^4K^2$, forms sparingly soluble needles, having a strong metallic lustre. After remaining for a few days under the exsiccator, it becomes anhydrous, the crystals, however, retaining their metallic lustre. The water which goes off is probably, therefore, not water of crystallisation, but hygroscopic water forcibly retained. The salt prepared from tetranitrochrysazin, exhibits the same remarkable relations to polarised light that were observed by Brewster in potassium chrysammate (i. 956). The observation of Haidinger that potassium chrysammate, when spread out on glass in thin layers in one particular direction, exhibits striking differences in the character of the reflected light, accordingly as the plane of reflection is parallel or perpendicular to that direction, is equally applicable to the potassium salt prepared from nitrochrysazin.

The **calcium salt**, $C^{14}H^{14}(NO^2)_4O^4Ca$, forms golden-yellow needles.

The **magnesium salt**, $C^{14}H^{14}(NO^2)_4Mg + 5H^2O$, forms splendid crystals, which have a red-gold lustre, give off their water at 160°, and turn gold-brown, but resume their original colour when moistened with water or breathed upon. According to Mulder (*Ann. Ch. Pharm.* lxxiii. 239), magnesiumchrysammate contains $6H^2O$ (19.6 per cent.); but this salt appears to have been but imperfectly air-dried. Liebermann a. Giesel

find only 5H²O (obs. 17.01 per cent.; calc. 16.91) for the air-dried salt, whether prepared from chrysammic acid or from tetranitrochryssazin.

The *barium salt* dried at 160° has the composition C¹⁴H⁴(NO²)²O⁴·Ba.

Acetyl-chryssazin, C¹⁶H⁶O⁴ = C¹⁴H⁴(OC²H³O²)²O⁴, is formed by heating chryssazin with acetic anhydride to 170°. It crystallises from alcohol in yellowish laminae resembling benzoic acid, is sublimable, and melts at 226°-230°.

With regard to the relative position of the two hydroxyl-groups in chryssazin, it is to be observed that the three modifications of dioxyanthraquinone, which have their two hydroxyls in the same benzene-group, are already known: viz. alizarin, quinizarin, and purpuranthin; consequently, chryssazin must have its two hydroxyls situated in different benzene-groups, as represented by the formula C¹⁴H⁴(OH).C²O².C²H²(OH). Now, as paracoumaric and para-oxybenzoic acid may be obtained in various ways from madder, it seems probable that chryssazin may be a condensation-product of para-oxybenzoic acid, just as anthraflavone (p. 107) is a condensation-product of oxybenzoic acid. The synthesis of chryssazin from para-oxybenzoic or paracoumaric acid has, however, not yet been effected (Liebermann u. Giesel).

8. *Frangula Acid*, obtained from the bark of *Rhamnus frangula*, has already been described (2nd Suppl. 584).

TRIOXYANTHRAQUINONES, C¹⁴H²O⁴.—Four of these compounds are now known, viz., Purpurin, Anthrapurpurin, Flavopurpurin, and Oxychryssazin.

1. *Purpurin*. This substance, originally obtained from madder (iv. 750), is also produced by direct oxidation of alizarin and of purpuroxanthin. 1 part of dry pulverised alizarin is mixed with 8 or 10 of sulphuric acid; 1 part of arsenic acid, or manganese peroxide, is added; and the whole is heated to 150°-160°, till a drop of the mixture thrown into dilute caustic soda gives the red coloration of purpurin. The whole is then poured into a large bulk of water, and the precipitate, after exhaustion with cold water, is dissolved in a saturated solution of alum, and then treated with an acid. The solution thus obtained deposits abundant flocculi of purpurin. The yield is rather large, though some loss is occasioned by the production (especially with arsenic acid) of a colouring matter, which dissolves in water to a yellowish-brown, and in alkalis to a red liquid (De Lalande, *Compt. rend.* lxxix. 669).

Purpurin is separated from alizarin by means of boiling alum-liquor, which dissolves the purpurin and leaves the alizarin. Commercial purpurin, however, still retains a certain amount of alizarin, besides other impurities. In a specimen which had been purified in Kahlbaum's works at Berlin, by solution of the crude product in boiling alum-liquor, Schunck and Roemer were able to detect traces of alizarin by the method described on the following page. But by again treating this product with boiling alum-liquor, adding acid to the filtered solution, and dissolving the precipitated purpurin in boiling alcohol, pure crystallised purpurin was obtained. Pure purpurin cannot be obtained by sublimation from the crude product, since alizarin sublimes at nearly the same temperature as purpurin.

Purpurin dissolves easily in boiling spirits of wine, forming a yellow solution, from which it crystallises on cooling in thin flattened prisms, sometimes 3 millims. long, having a deep orange colour and considerable lustre. On being heated to 100°, these crystals become dark red from loss of water. A solution of purpurin in strong alcohol deposits dark-red anhydrous needles.

Purpurin melts at 253°, but begins to sublime at 150° (according to Schützenberger at 250°). The sublimate consists of red, plumose, or needle-shaped crystals. Much carbonaceous residue is left. The crystals obtained by dissolving sublimed purpurin in spirits of wine are generally anhydrous, but occasionally hydrated crystals of the usual appearance are obtained. After purpurin has been repeatedly sublimed, its melting point becomes considerably depressed, indicating some kind of decomposition, but after recrystallising several times from alcohol, the melting point again becomes constant at 253°.

Purpurin is slightly soluble in boiling water, the solution having a yellow colour with a tinge of red, and depositing crystalline yellow flocks on cooling. It dissolves in ether, giving a yellow fluorescent solution, which shows the two bands of absorption described by Stokes (iii. 638, footnote). It also dissolves readily in boiling carbon disulphide, benzene and glacial acetic acid, yielding yellow solutions which deposit crystalline needles on cooling. These solutions show two bands of absorption coinciding with those of the ethereal solution. Purpurin dissolves in concentrated sulphuric acid, giving a rose-red solution, which shows three bands of absorption, one in the yellow, the others in the same position as those of the ethereal solution. It dissolves also in caustic potash and soda-ley, in sodium carbonate solution, and in ammonia; the solutions have a deep-red colour, inclining to purple, and show the absorption-bands described by Stokes and other observers. In alcoholic potash or soda, purpurin is almost insoluble. Treated with boiling baryta-water, it forms a

purple lake, quite insoluble in water. With lime-water it yields a compound which resembles that of barium, and is also insoluble.

Purpurin dissolved in caustic alkali is completely decomposed by oxidation on exposure to the air, the colour of the solution changing from purple to pale yellow. Alizarin, on the other hand, when similarly treated, remains unchanged. This reaction affords an easy method of detecting small quantities of alizarin in presence of purpurin. The mixture of the two is dissolved in caustic soda, and the solution is exposed to the air in a shallow vessel till it becomes nearly colourless, and no longer exhibits the absorption-bands of purpurin. The alizarin may then be precipitated by hydrochloric acid, dissolved in ether, and examined by the spectroscope, when its characteristic absorption-bands will be distinctly seen (Schunck & Roemer, *Chem. Soc. Jour.* 1877, i. 665).

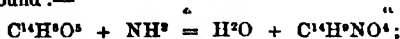
Purpurin dissolves in boiling alum-liquor, giving the well-known pink fluorescent solution, which, on cooling, generally yields a deposit, consisting of yellow (crystalline needles of purpurin mixed with amorphous particles of an alumina-compound, as may easily be seen on treating the deposit, after filtration, with boiling alcohol, which dissolves the purpurin with a yellow colour, leaving the alumina lake as a dark-red powder. The solution doubtless contains purpurin in combination with alumina; for, on agitation with ether, it remains quite unchanged, whereas, after the addition of hydrochloric acid, ether takes up purpurin, forming a yellow solution, and leaving the liquid below only slightly coloured. Nevertheless, the combination is a very loose one, for if alcohol be added to the solution, to precipitate the excess of alum present, and the filtrate be evaporated, a mixture of alum crystals and needles of purpurin is obtained, from which the purpurin may be extracted by treatment with absolute alcohol, no trace of any aluminous compound being observed in the residue. The solution in alum-liquor, when mixed with a little sodium carbonate or ammonia, the liquid still retaining an acid reaction, gives a flocculent precipitate, having the pink colour peculiar to the so-called madder lakes, which, as Robiquet showed long ago, are essentially compounds of purpurin with alumina. The precipitate is quite insoluble in a strong boiling solution of sodium carbonate, but dissolves easily in sodium hydrate.

An alcoholic solution of purpurin gives, with lead acetate, a dark crimson precipitate, which, on treatment with an excess of alcoholic lead acetate solution, dissolves, yielding a fine crimson solution, which shows three bands of absorption. This behaviour is characteristic, and may serve to distinguish purpurin from alizarin, which gives a lead-compound quite insoluble in alcoholic lead acetate.

An alcoholic solution of purpurin gives, with copper acetate, a dark reddish-yellow precipitate, whereas an alcoholic solution of alizarin becomes purple on the addition of copper acetate, and gives no precipitate, provided the alizarin is quite pure.

Purpurin, quite free from alizarin, heated in sealed tubes to 300° for several hours, is entirely decomposed, yielding a highly carbonised mass, from which boiling alcohol extracts quinizarin. The yield of this substance is but small, and is surpassed by that of the bye-products. To obtain the largest amount of quinizarin, it is best to discontinue heating before the purpurin is completely decomposed. The tube containing the latter having been heated to 300° for 6 or 7 hours, the contents are removed and treated with a boiling dilute solution of sodium carbonate, which dissolves a great part of the undecomposed purpurin, together with various bye-products. The residue is now treated with dilute caustic potash-ley, and the quinizarin and purpurin in solution are separated by passing through it a current of carbonic anhydride as long as any precipitate is formed. The precipitate contains quinizarin with a little purpurin, the latter being, for the most part, left in solution. The precipitate is filtered off and treated with hydrochloric acid, and the flocks left by the acid are again dissolved in caustic ley, carbonic anhydride being a second time passed through the solution. The process is repeated until the filtrate no longer contains purpurin.

Purpurin is reduced to purpuroxanthin by the action of phosphorus on its hot alkaline solution, or by first converting it into purpuramide (p. 111) by heating it to 150° with aqueous ammonia, and then passing nitrous acid vapour into the boiling alcoholic solution of this compound:—



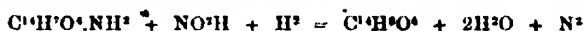
Purpurin is converted, by oxidation with nitric acid, into phthalic acid, and must therefore have its three hydroxyl-groups in the same benzene-group, as represented by the formula $\text{C}^6\text{H}^3\text{C}^3\text{O}^3\text{C}^6\text{H}(\text{OH})^3$.

Hydrate of Purpurin is precipitated on adding an acid to a solution of purpurin in an alkali or in alum-water (Rosenstiehl, *Compt. rend.* lxxix. 764).

Bromopurpurin, $C^{10}H^7BrO^4$, is formed by digesting purpurin at 150° – 200° in sealed tubes with carbon disulphide containing bromine. It crystallises from glacial acetic acid in dark red lustrous needles melting at 276° , resembles purpurin in most of its properties, but is less soluble in alcohol and glacial acetic acid, and sublimes when heated, leaving scarcely any residue.

Triacetylpurpurin, $C^{14}H^4(C^2H^3O)^3O^4$, first obtained by Liebermann & Giesel (*Deut. Chem. Ges. Ber.* ix. 332), is prepared by heating purpurin with acetic anhydride at 180° . When heated it begins to soften at 193° , and melts completely at 198° – 200° (Schunck & Roemer), at 190° – 193° (Liebermann & Giesel). It is decomposed even in the cold by dilute caustic potash-ley, yielding purpurin; dissolves in concentrated nitric acid, giving a yellowish-brown solution, which, on addition of water, deposits yellow flocks. These flocks dissolve in caustic potash-ley, giving a fine pink solution which shows the absorption-bands of purpurin (Schunck & Roemer).

Purpuramide, $C^{10}H^7NO^4 = C^{10}H^7O^4.NH^2 = C^{10}H^5 \left\{ \begin{smallmatrix} (O^2)^2 \\ NH^2 \\ (OH)^2 \end{smallmatrix} \right.$, is formed from purpurin by the action of ammonia in the same manner as alizaramide from alizarin. It crystallises in brown needles having a green metallic lustre. Its solution in alkalis is much redder than that of alizaramide. It is decomposed by nitrous acid in the same manner as alizaramide, yielding purpuroxanthin:



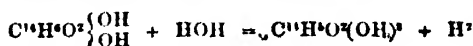
(Liebermann, *Lieb's Annalen*, clxxxiii. 145).

Pseudopurpurin.—This constituent of crude purpurin was originally regarded as a dioxypurpurin or trioxyalizarin, $C^{10}H^{10}O^3$ (alizarin being then represented by the formula $C^{10}H^8O^3$, *Ann. Chem. Phys.* (3) lxxiv. 561) that it is a purpurin being resolved by heat into CO^2 and purpurin:



This view of its constitution readily explains its conversion into purpurin by the action of alkalis even at ordinary temperatures, the change consisting simply in the abstraction of CO^2 .

2 and 3. **Anthrapurpurin** and **Flavopurpurin**. Anthrapurpurin was discovered by Perkin, who obtained it as a secondary product in the preparation of alizarin from anthraquinone (*2nd Suppl.* 88). It is produced by the action of caustic alkalis on anthraquinone-disulphonic acid, $C^{14}H^8O^2(SO^2H)^2$, this acid being first converted into the monosulphonic acid, $C^{14}H^8O^2 \left\{ \begin{smallmatrix} OH \\ SO^2H \end{smallmatrix} \right.$, the latter by the further action of the alkali into iso-anthraflavic acid (p. 105), and this finally into anthrapurpurin:



(Perkin, *Chem. Soc. Jour.* 1876, i. 851).

To prepare anthrapurpurin from iso-anthraflavic acid, the potassium salt of this acid is heated with caustic potash, whereupon the red colour of the liquid changes to violet, very quickly if the temperature be raised nearly to the melting point of potassium hydrate. When the depth of the violet colour no longer increases, the fused mass is to be dissolved in water and the solution supersaturated with hydrochloric acid; this throws down a yellowish gelatinous precipitate, which must be treated with cold baryta-water to remove unaltered iso-anthraflavic acid. The remaining lake, decomposed by hydrochloric acid, yields pure anthrapurpurin, which, by crystallisation from alcohol, may be obtained in long orange-coloured needles (Schunck & Roemer, *Deut. Chem. Ges. Ber.* ix. 678).

Flavopurpurin is produced in a similar manner from anthraflavic acid. This acid is less easily attacked by potash than iso-anthraflavic acid, and partial carbonisation is apt to take place. This, however, may be avoided by decomposing the acid

yellow needles.

The following table exhibits a comparison of the properties of these two isomeric bodies:—

Anthrapurpurin.

Orange-coloured needles. Anhydrous. Easily soluble in boiling alcohol. Slightly soluble in boiling water. Solution turns red on prolonged boiling.

Dissolves with difficulty in ether. Dissolves in boiling glacial acetic acid, and separates on cooling in stellate groups of needles.

Dissolves in strong sulphuric acid with red-violet colour.

Dissolves in potash-ley with violet colour, the tint, however, being redder than that of an alkaline solution of alizarin.

Sparingly soluble in hot baryta-water with violet colour.

The solution exhibits absorption-bands.

Soluble in ammonia, with violet-colour. The solution exhibits no bands.

Soluble in sodium carbonate, with violet colour.

Alcoholic lead acetate forms a purple precipitate, which, when boiled with excess of lead acetate, dissolves with violet colour.

Alcoholic cupric acetate forms a solution of a fine violet colour.

Slightly soluble in alum.

Melts above 330°.

Sublimes in orange-coloured needles.

Colours mordants.

The alkaline solution exhibits two absorption-bands having the same positions as those of an alizarin solution.

The triacetyl-derivative of the anthrapurpurin obtained from iso-anthraflavic acid exhibits exactly the same characters as that of the anthrapurpurin originally obtained by Perkin.

Flavopurpurin is very easily distinguished from the other tri-oxyanthraquinones by its spectrum.

From experiments by Caro it appears that anthraflavic acid and iso-anthraflavic acid are produced from two different anthraquinone-disulphonic acids by the moderated action of alkali; stronger reaction gives rise to anthrapurpurin or flavopurpurin. The action therefore takes place in the following phases:—

α-Anthraquinone-disulphonic Acid.

Anthraflavic acid.

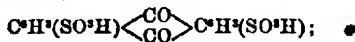
Flavopurpurin.

β-Anthraquinone-disulphonic Acid.

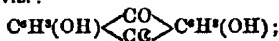
Iso-anthraflavic acid.

Anthrapurpurin.

Since alizarin, which contains both its hydroxyls in the same benzene group, is not produced by the action of alkalis on either of these anthraquinone-disulphonic acids, it may be inferred that in both of them the hydroxyls are situated in different benzene-groups, as represented by the formula:—



also that the isomeric anthraflavic acids formed from them by the action of alkalis have a similar constitution, viz.:—

*Flavopurpurin.*

Golden-yellow needles. Anhydrous. Easily soluble even in cold alcohol. Slightly soluble. Solution remains yellow when boiled.

The same.

The same.

Dissolves in strong sulphuric acid with red-brown colour.

Dissolves in potash-ley with purple colour, redder than anthrapurpurin, but not so red as purpurin. On dilution, or on addition of only slightly diluted alkali, the solution appears pure red. The colour disappears after long standing.

Sparingly soluble in hot baryta-water, with red-violet colour.

The solution exhibits absorption-bands when in thick layers.

Soluble in ammonia, with yellowish-red colour. The solution exhibits no bands.

Soluble in sodium carbonate, with yellowish-red colour.

Alcoholic lead acetate forms a red-brown precipitate, very sparingly soluble in excess of lead acetate, with red colour.

Alcoholic cupric acetate forms a red solution.

The same.

The same.

The same.

The same.

The alkaline solution likewise exhibits two absorption-bands, but somewhat farther from the red; also a broad stripe in the blue.

and that the trioxyanthraquinones, anthrapurpurin, and flavopurpurin are constituted according to the formula :



the difference between them probably arising from the different relative positions of the two hydroxyls which are situated in the same benzene nucleus.

Oxychrysazin is formed by heating the red alkaline solution of chrysazin with potash, whereby it is converted into a bright blue mass, having a splendid metallic lustre and dissolving in water with a blue-violet colour, like that of alizarin. From this solution acids precipitate the oxychrysazin in brown flocks, which may be purified by crystallisation from alcohol. With mordants it forms very bright colours intermediate between those produced by alizarin and by purpurin.

Oxychrysazin resembles anthrapurpurin in being precipitated for the most part from its solution in sodium carbonate by agitation with alumina. The triacetyl-derivatives of these three isomeric compounds obtained by heating them with acetic anhydride to 170° exhibit the following characters :

Triacetyl-oxychrysazin :—Light-yellow needles, melting at 192°-193°.

Triacetyl-purpurin :—Yellowish needles melting at 190°-193°.

Triacetyl-anthrapurpurin :—Melts at 220°-222° (Perkin).

So far as these characters go, oxychrysazin might be identical with purpurin ; but the two substances are immediately distinguishable by the colour of their alkaline solutions, purpurin giving a red, and oxychrysazin a blue solution, and by their optical characters. Purpurin, whether in alkaline solution or in its strongly fluorescent alum-solution, gives, when examined by the spectroscope, very characteristic absorption-bands, which are not exhibited by oxychrysazin.

TETRAOXYANTHRAQUINONES, $C^{14}H^4(OH)^4O^2$.—Two of these compounds are known, viz., anthrachrysone, produced by oxidation of anthracene and of its dichloro- and dibromo-derivatives (1st Suppl. 180), and

Rusopin, produced by heating opianic acid (iv. 206) with strong sulphuric acid to 180°. This substance crystallises in yellowish-red needles or crusts ; decomposes to a great extent when sublimed ; is slightly soluble in boiling water, moderately soluble in boiling alcohol, easily in glacial acetic acid, slightly in ether. In alkalis it dissolves with violet-red, in ammonia with red-brown colour. The ammoniacal solution gives violet-red precipitates with the chlorides of barium and calcium. When heated with zinc-dust it yields anthracene (Liebmann a. Chojnacki, *Deut. Chem. Ges. Ber.* iv. 637 ; *Liebig's Annalen*, cxlii. 322).

HEXAOXYANTHRAQUINONE, $C^{14}H^4O^6$. The only known body of this composition is rufigallie acid, $C^6H^4(OH)^2 \cdot C^8O^2 \cdot C^6H^4(OH)^2$, obtained by heating gallic or digallic acid with strong sulphuric acid (iv. 133 ; 1st Suppl. 999 ; 2nd Suppl. 1062).

ANTHRAQUINONE-CARBONIC ACID, $C^{14}H^4O^4 - C^6H^4O^2 \cdot CO^2H$. This acid is formed by oxidation of β -anthracene-carbonic acid (Liebmann a. vom Rath, p. 96), also by oxidation of methylantracene with chromic acid (Weiler, p. 96). It crystallises from alcohol in compact brilliant yellow prisms melting at 282°-284°. Its barium salt forms microscopic needles, the calcium salt scales ; the lead salt is insoluble. The sodium salt is insoluble in caustic soda. The acid when carefully heated sublimes in yellow needles, but at a stronger heat it is resolved into anthraquinone and carbon dioxide (Liebmann a. vom Rath). Boiled with zinc-dust and potash or soda, it forms a red solution like anthraquinone, and when heated with soda-lime it yields the latter compound (Weiler).

ANTHRAQUINONE-DISULPHONIC ACID, $C^{14}H^4(SO^2H)^2O^2$. This acid may be formed by heating β -benzoylbenzoic acid with fuming sulphuric acid till the resulting liquid no longer gives a precipitate with water. The reaction may be expressed by the equation :



(Liebmann, *Deut. Chem. Ges. Ber.* vii. 805).

ANTHROLE. See ANTHRAPHENOLS (p. 97).

ANTIMONY. The 'explosive' antimony deposited at the negative pole on electrolysing a hydrochloric acid solution of antimonious chloride (i. 315 ; 1st Suppl. 181) has been found by Böttger to contain occluded hydrogen as well as antimony chloride (*Chem. Centr.* 1875, p. 674).

Estimation.—Houzeau (*Compt. rend.* lxxv. 1828) estimates small quantities of

ANTIMONY.

Antimony by a volumetric method founded on the precipitation of silver by antimonetted hydrogen (stibine), the reaction taking place according to the equation :



By titrating the quantity of silver remaining in solution with a normal solution of sodium chloride, the quantity of silver precipitated may be determined, and thence the quantity of antimony.

R. F. Smith (*Deut. Chem. Ges. Ber.* iv. 855) treats finely pulverised antimony ores with hot hydrochloric acid, precipitates the antimony from the solution of the chloride with zinc or iron, and fuses the metal under a layer of charcoal powder.

On the Estimation of Antimony in Type-metal see R. Bartley (*Dingl. pol. J.* ccxviii. 270; *Chem. Soc. Jour.* 1876, i. 748). On the Separation of Antimony from Tin see Winckler (*Zeitschr. Annal. Chem.* xiv. 156; *Chem. Soc. Jour.* 1876, i. 748).

Tribromide, SbBr³. This compound may be prepared by distilling a mixture of antimony sulphate and potassium bromide. When decomposed by cold water it yields an oxybromide, Sb³Br²O³, or 2SbBr³.5Sb²O³. Hot water effects a more complete decomposition, resulting in the compound SbBr³.10Sb³Br²O³. By washing this substance with carbon sulphide, the tribromide is dissolved out, and the compound Sb³Br²O³ remains (W. E. Macivor, *Chem. News*, xxix. 179).

Antimony Chlorides. 1. *Trichloride, SbCl³.*—A concentrated hot solution of antimony trichloride diluted with boiling water until the oxychloride begins to be precipitated, and then left to cool, after addition of a drop or two of strong hydrochloric acid, solidifies to an amorphous mass of oxychloride, which liquefies on warming, and gives on analysis numbers corresponding with those required by Sabanejeff's oxychloride, Sb³Cl²O³, or 2SbCl³.5Sb²O³. When hot concentrated hydrochloric acid is saturated with antimonious oxychloride, an oxychloride containing less chlorine separates on cooling (Macivor, *Chem. News*, xxxii. 229).

Reaction with Hydrocarbons.—When the mixed vapours of SbCl³ and benzene are passed through a red-hot tube, diphenyl is formed, according to the equation :



This yield, however, is much below the theoretical quantity. With *naphthalene* in like manner, isodinaphthyl is produced. (See DIPHENYL and DINAPHTHYL.) With *toluene* much hydrochloric acid was evolved and much antimony reduced; and a tarry mass was obtained, which, on distillation, yielded no stilbene, but at 270°, 280°–300°, and about 350°, rancid smelling oils, the last of which solidified to a mass of striated crystals (Watson Smith, *Chem. Soc. Jour.* 1876, ii. 30).

2. *Pentachloride, SbCl⁵.*—This compound acts energetically on many organic bodies, the pentachloride itself splitting up into antimony and the trichloride, and the organic matter being either chlorinated by the free chlorine, or completely charred by the dehydrating action of the pentachloride. By properly regulating the action, however, it is possible to obtain direct addition-compounds of the pentachloride with various alcohols and with ethyl oxide; and several of these compounds have been prepared by W. Earleton Williams (*Chem. Soc. Jour.* 1876, ii. 463).

With *Ethyl Alcohol, SbCl⁵.C²H⁵O.*—This is a white crystalline hygroscopic substance formed by slowly adding absolute alcohol to antimony pentachloride contained in a wide glass tube surrounded by cold water. It is instantly decomposed by water, with formation of alcohol and antimonic acid, but dissolves easily and without decomposition in aqueous tartaric acid, also in alcohol, ether, and chloroform, and is easily purified by recrystallisation from alcohol, separating from the hot saturated solution, on cooling, in splendid white needle-shaped crystals, apparently belonging to the orthorhombic system. It melts at 66°–67°, is completely decomposed by distillation, and undergoes gradual alteration even when kept in sealed tubes. When heated in a sealed tube to 110°–115° for four hours, it is converted into a dark brown liquid which deposits a few crystals of antimony trichloride, and is resolved by distillation into hydrochloric acid, ethyl chloride, and antimony trichloride, with a small residue of antimony trioxide and organic matter.

With *Methyl Alcohol, SbCl⁵.CH³O.*—This compound is prepared like the preceding, which it resembles in its properties. It is deposited from a hot alcoholic solution in leafy or tabular crystals having a faint yellow colour, and melting at 81° to a yellow liquid which decomposes at 130°, with evolution of hydrochloric acid and methyl chloride. It is more stable than the ethyl-compound, and may be preserved without alteration in well-stoppered bottles.

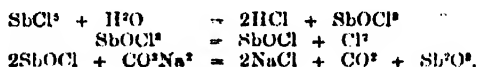
With *Amyl Alcohol.*—This compound is less stable than either of the preceding, and is difficult to prepare, as amyl alcohol acts with great violence, even on frozen

antimony pentachloride. It forms white star-like crystals, often discoloured by the decomposed alcohol.

With Ethyl Oxide, $\text{SbCl}_5 \cdot \text{C}_2\text{H}_5\text{O}$.—This compound is best prepared by mixing the two substances in the proportion of their molecular weights, keeping the mixture well cooled, as decomposition takes place at 70° . The compound when freshly prepared is a finely-divided crystalline powder of a greyish-white colour. It is very hygroscopic and is decomposed by water, but dissolves without alteration in alcohol and in ether. The crystals melt at 68° – 69° and are very unstable, blackening spontaneously even at ordinary temperatures, and decomposing when heated for a few minutes to their melting point.

3. *Oxychloride*, SbOCl .—This compound, analogous to POCl_3 , not hitherto described, has been obtained as follows by Daubrawa (*Liebigs Annalen*, clxxxvi. 110). 16 parts of antimony pentachloride are added drop by drop to 1 part of water cooled by ice. A yellowish crystalline mass is thus obtained, which remains unaltered in dry air, melts when heated to a clear yellowish oily liquid, and finally boils, giving off dense vapours, and becoming white and opaque when cold. These results indicate that the body when heated splits up into SbOCl and Cl_2 , the chlorine escaping. No water is deposited in the colder part of the tube, a proof that the elements of water are entirely absorbed in the chemical reaction. When treated with a larger quantity of water, it is converted into a white pulverulent substance, Frémy's pyroantimonious acid.

On shaking the oxychloride with a concentrated solution of sodium carbonate, a momentary evolution of gas took place, and a bulky white precipitate was formed, which became granular on prolonged boiling, the change being attended with further evolution of gas. The precipitate washed with dilute nitric acid and dried was found to consist of antimonious oxide, Sb_2O_3 . Hence it appears probable that the formation and decomposition of the oxychloride take place as represented by the following equations:



The oxychloride dissolves readily in alcohol to a clear liquid, which, when evaporated on the water-bath, gives off hydrochloric acid, and ultimately yields a mass of light yellow crystals grouped in rosettes. On adding water to the residue, a smell of alcohol is developed and a white precipitate thrown down, possibly from decomposition of a triethyl antimonate, formed in the first instance, with evolution of alcohol and separation of antimonious acid (Daubrawa).

Antimony Iodides (Macivor, *Chem. Soc. J.* 1876, i. 328). The *tri-iodide*, SbI_3 —for the preparation of which see 1st Suppl. 186—has, when cast into bars, a dull semi-metallic lustre on the outer surface, but when broken, exhibits a beautifully radiated fracture and a bright semi-metallic lustre. It melts at 164.4° (corr.) to a red liquid, and boils at a higher temperature, evolving orange-coloured vapours, which in an atmosphere of hydrogen or carbon dioxide, condense on a cold surface in large, thin, transparent, poppy-red, hexagonal plates, similar to those obtained by Schneider (*loc. cit.*) If, however, the sublimation be conducted in air, the iodide is partly decomposed, with liberation of iodine and formation of antimonious oxide. In dry oxygen the decomposition is more complete, the antimony burning with flame. The tri-iodide yields a reddish-brown powder permanent in the air, and soluble in carbon sulphide and in boiling benzene, forming yellow solutions, which, on evaporation, deposit the red tabular crystals described by Nicklès (*loc. cit.*) It dissolves partially also in carbon trichloride at about 250° . It is almost insoluble in chloroform, and does not dissolve in carbon tetrachloride or in oil of turpentine.

Antimonious iodide dissolves readily in aqueous *hydriodic acid*, and the solution when poured into water, gives a yellow precipitate of oxyiodide. The solution of the iodide in cold *hydrochloric acid* contains undecomposed iodide, and consequently gives a yellow precipitate with water, but after a few minutes' boiling, the whole of the antimony is converted into trichloride, and the solution then gives with water a white precipitate of oxychloride. The iodide digested with *absolute alcohol* partly dissolves without decomposition, but the greater part is converted into the yellow oxyiodide. *Anhydrous ether* also produces oxyiodide and a dark-coloured solution containing undecomposed tri-iodide. Cold dilute *sulphuric acid*, ($2\text{H}^+\text{SO}_4 + 18\text{H}_2\text{O}$), contrary to the statement of Brandes, has little or no action on antimonious iodide, but on applying a gentle heat, rapid decomposition takes place, with evolution of iodine and formation of antimonious sulphate. Nitric acid of sp. gr. 1.5 decomposes

the iodide immediately, converting it into oxide; acid of sp. gr. 1.4 acts in the same manner; acid of sp. gr. 1.2 after some time only. *Chlorine* at once converts the tri-iodide into trichloride, and iodine monochloride; *bromine* acts in like manner. *Iodine monochloride* produces antimonious chloride and free iodine (Macivor, *Chem. Soc. J.* 1876, i. 328).

The oxyiodide, formed as above mentioned by the action of water, alcohol and ether, on the tri-iodide, varies in composition according to the particular circumstances under which its formation takes place. When formed by pouring the hydriodic acid solution of the iodide into boiling water, it has the composition $\text{Sb}^4\text{I}^2\text{O}^3$ or $2\text{SbI}^4.5\text{Sb}^2\text{O}^3$. It dissolves somewhat slowly in tartaric acid; when strongly heated it is resolved into tri-iodide and trioxide.

The pentiodide of antimony described by van der Espt (1st. *Suppl.* 187), as formed by heating iodine and antimony together in the required proportions, appears to be nothing but a mixture of the tri-iodide with free iodine.

A Phosphide, PSb, is obtained by the action of phosphorus on antimony tribromide, both being dissolved in carbon sulphide. It is a red powder, insoluble in benzene, ether, and carbon sulphide (W. Ramsay, *Deut. Chem. Ges. Ber.* vi. 1362).

On the *Oxides and Acids of Antimony*, and the probable existence of an *Ortho-antimonic acid*, SbO^4H^3 , analogous to PO^4H^3 , see Daubrawa (*Liebig's Annalen*, cxxxvi. 110).

A phosphide, Sb^2S^3 .—According to Terreil (*Compt. rend.* lxxviii. 1500), native antimonious sulphide is not acted on by pure potassium carbonate (prepared by precipitating a solution of pure potassium sulphate with caustic baryta, and passing carbon dioxide into the liquid) in aqueous solution; and the formation of kermes (amorphous trisulphide containing oxide) from the native sulphide by the action of potassium carbonate prepared from cream of tartar or from the bicarbonate is due to the presence of small quantities of sodium carbonate. Terreil, therefore, recommends the formation of kermes in the wet way as a test for the presence of sodium carbonate in potassium carbonate. In the dry way, on the contrary, the yield of kermes is greater with carbonate of potassium than with carbonate of sodium. Milk of lime acts but slightly on antimonious sulphide; the hydroxides of barium and strontium not at all.

This mineral, to the amount of several units per cent., is almost always found in nugitic greenstones, and is frequently met with in other plutonic rocks, especially trachytes and lavas (Petersen, *J. pr. Chem.* [2], vi. 197). It also occurs in many dolerites, in colourless hexagons and long needles (Sandberger, *Jahrb. f. Min.* 1874, 88).

Apatite is found on the south coast of Norway, between Langesundfjord and the town of Arendal, in veins, the most important of which occur at Oedegarden, in the parish of Bamle, in gabbro rock. This rock has a spotted appearance and consists of hornblende and labradorite, intersected by veins of a magnesia-mica containing apatite. At Persdal the vein-mass in the gabbro is magnetic iron-pyrites, and in it lie many crystals of apatite, exhibiting the characteristic rounding off of the angles and edges. At Kragerø apatite does not occur in gabbro, but in vein-stocks of hornblende, the centre of the vein consisting principally of coarse radiating hornblende, which often encloses masses of apatite two feet long. These Kragerø veins have a most peculiar and beautiful appearance, being composed of intensely black hornblende, red apatite, light green and grey radiating masses of asbestos-steatite, and rutile. The other veins are either hornblende or granite. It appears that apatite crystals are generally found only in the hornblende veins which contain magnetic iron-pyrites. It has, however, been found crystallised in quartz-masses which intersect the layers of hornblende and micaceous schist of Oestre Kjørrestad, in the parish of Bamle; sometimes in crystals two inches long, exhibiting the combination $\infty \text{P.O.P.P.}$ Apatite crystals from Oexoiekollen (Snarum) exhibit the combination $\infty \text{P.} \infty \text{P}^2. \text{OP. R. } 2\text{P}^2$; the variety called moroxite found at Aestesvåg is found in beautiful large crystals, on which the basal terminal plane does not occur; the colours are white, grey, yellow, green, violet, brick-red. The apatite from Oedegarden is penetrated, and coloured by a peculiar carbonaceous substance (Brügger a. Reusch, *Jahrb. f. Min.* 1876, 196).

Crystalline deposits and small distinct crystals of apatite have been formed on small cleft faces of a rather hard osteolite, occurring on the base of the Rossberg in the northern Odenwald (Petersen, *ibid.* 1873, 852).

Apatite also occurs, together with hyalite and arragonite, in the neighbourhood of Waltzsch in Bohemia. The apatite and hyalite occur most frequently in druses, the apatite forming the lowest layer; then follow hyalite and apatite alternately; and the uppermost layers are formed of hemispherical and botryoidal concretions, consisting of apatite and scales of hyalite, or of an intimate mixture of the two

minerals having an opalescent aspect. Hyalite occurs also in the basalt of Waltusch in scaly-fibrous forms which are pseudomorphs after apatite, and in radial groups of needles which are pseudomorphs after arragonite.

Splendid crystals of apatite have lately been formed at Untersulzbach, often enclosing fine needles of hornblende, but sometimes perfectly colourless and transparent; tabular through OP. One of them had a breadth of 5 cm., another of 8 cm., caused by the parallel growth of two individuals (Tschermak, *Jahrb. f. Mineralogie*, 1876, 200).

Fluor-apatite from Murcia, in perfectly transparent greenish-yellow crystals, of sp. gr. 3.25, was found by Church (*Chem. Soc. J.* [2], xi. 101) to contain :

Ca^{10}O^*	CaCl^*	CaF^*	H^2O	X^*
93.11	1.12	4.45	0.19	1.13 = 100.

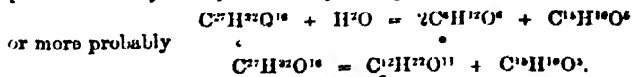
The percentage of tricalcic phosphate in this fluor-apatite is nearly 1 per cent. higher than that (92.26) required by the formula $\text{Ca}_3(\text{PO}_4)_2\text{F}$.

APHROSIDERITE. Sandberger's analysis of this mineral represents the whole of the iron as existing in the state of ferrous oxide (i. 349). According to Nies, however (*Chem. Cent.* 1875, 127; *Jahrb. f. Min.* 1873, 320), this is not the case, as both oxides of iron enter into the composition of the mineral, which may, in fact, be represented by the formula $8(2\text{RO} \cdot \text{SiO}_2) + 5(\text{R}^2\text{O}^3 \cdot \text{SiO}_2) + 18\text{H}^2\text{O}$, where RO represents ferrous oxide and magnesia, R^2O^3 ferric oxide and alumina, the ratio of $\text{FeO} : \text{MgO}$ being about 10 : 1, and that of $\text{Al}^2\text{O}^3 : \text{Fe}^2\text{O}^3 = 5 : 1$. From a comparison of the analyses by various chemists of 'Aphrosiderite,' or of 'minerals related to aphrosiderite,' Nies concludes that the greater number cannot be made available for the determination of the formula, on account of imperfect separation and determination of the two oxides of iron; and that those in which the two oxides were exactly separated and estimated, relate to minerals specifically different from aphrosiderite. On the other hand, he considers it most probable that the true aphrosiderite is identical with Breithaupt's thuringite (v. 791).

APIIN. This name was given by Braconnot to a substance first obtained by Rump in 1836 (Buchner's *Repert. f. Pharm.* vi. 6), from the leaves, stalks, and seeds of common pursley. It was afterwards examined by v. Planta and Wallace, who obtained it only in an impure state, as a gelatinous mass (i. 350), and more exactly by Lindenhorn (*Inaugural Dissertation*, Würzburg, 1867), who obtained it, by careful evaporation of the alcoholic solution, in needles which gave by analysis 54.71–55.26 per cent. carbon, and 5.49 to 5.60 hydrogen, and further showed that it is a glucoside, splitting up, when boiled with dilute sulphuric acid, into glucose and apigenin (66.13 per cent. C. 3.9 H.) From these numbers Lindenhorn inferred that apigenin is isomeric with quinine, and assigned to apiin the formula $\text{C}^{27}\text{H}^{40}\text{O}^7$, representing its decomposition by the equation, $\text{C}^{27}\text{H}^{40}\text{O}^7 + \text{H}^2\text{O} = \text{C}^6\text{H}^{12}\text{O}^5 + \text{C}^{21}\text{H}^{28}\text{O}^2$.

Quite recently apiin has been further examined by E. v. Gerichten (*Deut. Chem. Ges. Ber.* ix. 1121), whose results agree in the main with those of Lindenhorn, his analysis of apiin giving 53.55 per cent. C., 5.36 H., and that of apigenin 66.12–66.21 C. and 3.75–3.91 H. He finds that apigenin is oxidised by chromic acid mixture, even at ordinary temperatures, to formic and carbonic acids, and by nitric acid to oxalic and picric acids.

By fusion with potash it yields phloroglucin, $\text{C}^{11}\text{H}^{10}\text{O}^7$, together with an acid not yet fully examined, which by further fusion with potash is converted into protocatechuic acid, $\text{C}^7\text{H}^6\text{O}^4$, small quantities of oxalic, formic, and paraoxybenzoic acids being formed at the same time. Apigenin must therefore contain at least 13 atoms of carbon. The analytical results cannot, however, be correctly represented by any 13-carbon formula, and the formula which agrees best with all the results is $\text{C}^{27}\text{H}^{40}\text{O}^7$ (C = 66.6; H = 5.2), and this gives for apiin the formula $\text{C}^{27}\text{H}^{42}\text{O}^{10}$ (C = 52.9; H = 5.2). With these numbers the decomposition of apiin by dilute sulphuric acid may be represented by the equation :



Apiin is slightly soluble in cold, easily in hot water, still more easily in hot alcohol, insoluble in ether; from the aqueous or alcoholic solution it always separates by slow cooling in the form of a jelly. It dissolves in alkalis with light yellow colour. Its hot aqueous solution gives no precipitate with silver nitrate, lead nitrate,

or copper sulphate, a brown-red precipitate with ferric chloride, a blood-red coloration with ferrous sulphate.

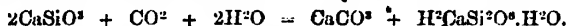
Apiin is the most powerfully dextrogyrate of all known substances, its specific rotatory power for yellow light being $+173^\circ$. The crystals melt at 228° (uncorrected).

APIOL, or **PARSLEY CAMPHOR**, is a crystalline substance, extracted, together with a liquid terpene, by distilling parsley-seeds with water. It forms long, white, brittle needles, melting at 30° and boiling at about 300° . By boiling it with alcoholic potash, it is converted into a body which crystallises in pearly, rhombic plates melting at 53.5° , and contains, as a mean of three analyses, $C=66.4$, $H=5.5$. This last body boiled with dilute nitric acid yields oxalic acid, and a substance which crystallises from alcohol in long, brilliant yellow needles, melting at 114° , and dissolving gradually in boiling potash with deep purple colour (v. Gerichten, *Deut. Chem. Ges. Ber.* ix, 1477).

APOMORPHINE. See MORPHINE.

APOPHYLLITE. *Formation from Wollastonite.*—A. Strangl (*Jahrbuch für Mineralogie*, 1875, 393), describes a specimen of wollastonite from Aserbach in Saxony, covered with a thin crust of apophyllite, which has evidently filled a cleft in the wollastonite, this cleft, however, not having been completely filled up by the apophyllite, excepting in a few places, so that most of the crystals of the latter project into the free cavity. These crystals are from 1 to 2 millimeters in size, perfectly colourless, strongly lustrous, and exhibit the (quadratic) combination $\infty P \infty \cdot OP \cdot P$, with ∞P very subordinate. They are either shortly prismatic, in which case P appears as a truncation of the combination-edges of $\infty P \infty$ and OP ; or they form thick plates, ∞P then appearing as a narrow truncation of the lateral edges of P .

This apophyllite has evidently been formed by the action of carbonic acid water on the wollastonite, forming calcium carbonate, which remained behind (the wollastonite effervesces with acids), and hydrated calcium silicate, which dissolved, and was deposited in the clefts of the wollastonite:—



APPLES. Apples when heated with water give off a considerable quantity of gas. Four of middle size yielded 100 c.c., consisting of 40.2 carbon dioxide, 59.37 nitrogen, and 0.43 oxygen. The apples contain, therefore, only carbon dioxide and nitrogen, the small quantity of oxygen being due to the presence of a little air. Older apples contain in proportion less carbon dioxide, in one case 31.07 being found to 68.93 of nitrogen (C. Bender, *Deut. Chem. Ges. Ber.* viii, 112).

AQUA REGIA. See NITROSYL CHLORIDES.

ARABIN (Scheibler, *Deut. Chem. Ges. Ber.* vi, 1124). Scheibler, in 1868, described a constituent of the cellular tissue of the sugar-beet, which, under certain circumstances, passes into the juice, and seriously hinders the formation of crystallisable sugar.* This substance possesses all the properties of the metaplectic acid, which Frémy obtained from the sugar-beet (iv, 369), excepting that its alkali-metal salts are not immediately precipitated by neutral or basic lead acetate, but only on addition of ammonia, and that, instead of being optically inactive, it is strongly laevogyrate.

Further investigation has shown that this substance is identical, not with metaplectic acid, but with arabic acid, $C^{12}H^{22}O^{11}$. The carbohydrate from beet and from gum-arabic, differ, indeed, only in their rotatory power, that of the former being $[\alpha] = -98.5$, that of the latter -36 (Béchamp). Scheibler finds, however, that the different varieties of gum-arabic occurring in commerce exhibit great diversities in their optical rotatory powers, not only in magnitude, but even in direction, and that similar diversities are exhibited by the carbohydrates from beets of different growths. But these bodies, though optically different, yield, when boiled with dilute acids, one and the same crystallisable laevogyrate sugar, called arabinose, having the composition $C^5H^{10}O^5$, together with a smaller quantity of an uncrystallisable dextrogyrate sugar, the relative quantities of the two sugars varying with the optical characters of the original substance.

Arabic acid is prepared from beet as follows: The fresh pulp is freed as much as possible from juice by pressure, then exhausted several times with alcohol of 86-90

* See First Supplement, p. 802, where on line 13 from the bottom, for turnip-pulp read pulp or marc of sugar-beet.

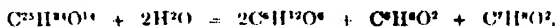
per cent., again pressed, then treated with warm milk of lime, and pressed once more, the excess of lime precipitated by carbonic acid, and the filtrate acidulated with acetic acid, and mixed with alcohol. The viscid gum thereby separated is purified by repeated solution in water, and finally, by fractional precipitation with alcohol. The arabin is thus precipitated in flocks, but even after repeated dissolution and re-precipitation, it is still not quite free from mineral matters.

Another kind of gum is obtained from beet juice which has passed into the state of mucous fermentation. On mixing this juice with alcohol, mannitic acid, lactic acid and a peculiar sugar remain dissolved, and a precipitate is obtained consisting of so-called 'fermentation gum,' which is dextrogyrate; forms with Fehling's solution a blue flocculent precipitate, and when boiled with dilute acids, yields an uncrystallisable sugar which reduces copper solutions (Scheibler).

Pararabin.—This is a modification of arabin, distinguished by not yielding sugar when treated with dilute acids. It is prepared from carrots or beet-root by pressing them well, exhausting the pulp with water and alcohol, digesting the residue with dilute hydrochloric acid (1 per cent.) for some hours, and then boiling, and precipitating with alcohol. The pararabin thus precipitated forms with water a jelly which dissolves in acids, but is completely precipitated by alkalis and by alcohol. By heating with an alkali it is converted into ordinary arabin. Pararabin forms with lead and barium the compounds $(C^{12}H^{10}O^{11})^2Pb$ and $2C^{12}H^{10}O^{11}Ba + 3H_2O$. It constitutes the Chinese vegetable jelly, called 'Agur-agur' (i. 61; E. Reichardt, *Deut. Chem. Ges. Ber.* viii. 807).

ARABINOSE, $C^6H^{12}O^6$. This kind of sugar, prepared from arabin as above described, crystallises, according to Groth, in well-formed rhombic prisms, exhibiting the combination ∞P , $\infty P\infty$, $P\infty$, sometimes also with ∞P^2 , $\infty P\infty$ [a very large], and $\infty P\infty$ subordinate. Angle ∞P : $\infty P = 111^\circ 44'$; ∞P : $\infty P\infty = 124^\circ 12'$; $P\infty$: $P\infty = 127^\circ 20'$; $P\infty$: $\infty P\infty = 116^\circ 20'$. Ratio of axes a : b : $c = 0.6783$: 1: 0.4436.

ARBUTIN. This glucoside, when heated with acids or ferments, has hitherto been supposed to yield only sugar and hydroquinone, according to the equation, $C^{12}H^{14}O^7 + H_2O = C^6H^{12}O^6 + C^6H^4O^2$ (1st Suppl. 191); but from recent experiments by Hlasiwetz u. Habermann (*Wien. Akad. Ber.* 1875, 73; *Licht's Annalen*, clxxvii. 339), it appears that, in addition to these compounds, methyl-hydroquinone, $C^7H^{10}O^2$, is likewise formed. Moreover, a careful revision of the published analyses of arbutin has shown that its composition is correctly represented by the formula, $C^{22}H^{30}O^{14}$, and, consequently, that the decomposition above mentioned takes place in the manner shown by the equation:



Strecker's *durum-arbutin* has, according to Hlasiwetz u. Habermann, the formula, $C^{22}H^{32}(NO^2)^2O^{14} + 3\frac{1}{2}H_2O$, with which, in fact, Strecker's numbers agree nearly.

ARDENNITE. This name is given by Lasaulx (*Jahrbuch f. Mineralogie*, 1872, 930; 1873, 124) to a silico-aluminate of manganese containing vanadic acid and sometimes also arsenic acid, which occurs near Ottreg in the Belgian Ardennes, mostly in thick-fibred cauliflower groups without recognisable crystalline forms, but exhibiting two directions of distinct cleavage. Small well-defined crystals are also found, which, according to measurements by vom Rath, belong to the rhombic system, being derived from a rhombic octahedron in which the axial ratio is

Brachydiagonal.	Macrodiagonal.	Principal axis.
0.4663	1	0.8135.

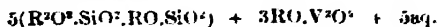
Observed faces: P , P^2 , ∞P , ∞P^2 , ∞P^2 , $P\infty$, $\infty P\infty$. Cleavage perfect parallel to $\infty P\infty$, distinct parallel to ∞P .

The colour of the mineral is colophony-brown, often also of a somewhat lighter yellowish colour; translucent with reddish colour in thin splinters; lustre, waxy. Sp. gr. = 3.620. Melts before the blowpipe to a black glass, and gives a manganese bead with borax.

Quantitative analysis of a dark-coloured variety gave the following numbers:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	V ₂ O ₅ .	Cu + PbO.	H ₂ O.
29.74	23.50	1.94	25.96	2.04	3.42	9.10	trace	4.04

agreeing nearly with the formula:



The lightest-coloured varieties contain arsenic as well as vanadium. Pisani

(*Compt. rend.* lxxv. 1542) found in a yellowish-brown variety (called by him *dew-alquite*):—

SiO ²	Al ² O ³	Fe ² O ³	MnO	CaO	MgO	CuO	V ² O ⁵	H ² O
28·70	28·36	2·94	26·40	4·30	4·32	1·30	1·80	0·98 = 99·10;

and in a subsequent analysis, 3·12 per cent. = V²O⁵ and 6·05 As²O³.

v. Lasaulx, by a further examination of the mineral (*Jahrbuch*, 1874, 276; 1876, 253; *Chem. Soc. Jour.* 1877, i. 54), finds that it exhibits several varieties, in which arsenic and vanadic acid replace each other isomorphously. The darkest-coloured specimens, with which his former analyses were made, were found to be quite free from arsenic, and to give, as before, 9·10 per cent. V²O⁵, whereas a lighter-coloured variety, of sp. gr. 3·662, gave 6·64 per cent. As²O³ and 28·82 per cent. silica, agreeing very nearly with Pisanì's determination, viz. 28·40 per cent. A somewhat darker variety, intermediate in colour between the two just mentioned, gave 2·98 per cent. As²O³. It is highly probable that, among the numerous varieties of the mineral, some may be found in which vanadium is altogether absent. Phosphoric acid, a trace of which was found in the first analysis made by v. Lasaulx, may perhaps be found in other varieties, replacing to a greater or less extent the arsenic and vanadic acids. See also Bettendorff (*Pogg. Ann.* clx. 126; *Chem. Soc. Jour.* 1877, ii. 175).

The water in ardenite is very intimately combined, and can be expelled only by strong and prolonged ignition.

In this respect, and likewise in its crystalline form, ardenite exhibits a considerable resemblance to ilvaite. The quantities of silica and alumina (or its equivalent in ferric oxide) also agree very nearly; but the quantities of manganous oxide, or its equivalent in ferrous oxide, differ considerably in the two minerals. Moreover ilvaite does not contain vanadium.

Ardenite occurs on a quartz vein of the crystalline slate near Ottrege, associated with smoke-grey quartz, which is traversed by pyrolusite, violet and black compounds of manganese and iron, and crystalline aggregates of albite. None of these minerals contain a trace of vanadium, which element is, therefore, an essential constituent of ardenite.

ARICINE. See CINCHONA ALKALOIDS.

ARNICA. The root of *Arnica montana* was examined in 1860 by Walz, who obtained caproic and caprylic acids from the watery distillate, and hexyl caproate from the essential oil (*1st Suppl.* 192). It has lately been examined by O. Sigel (*Liebig's Annalen*, clxx. 345), who has arrived at totally different results.

The essential oil was distilled from a mixture of old and fresh arnica root. The water which accompanied the oil was strongly acid. It was neutralised with sodium carbonate, evaporated to dryness, exhausted with alcohol, the alcoholic solution evaporated again to dryness, and the acid separated by distillation with sulphuric acid. The distillate had a pungent odour, which was afterwards found to be due to formic acid, but it also smelt of butyric acid. It was neutralised by ammonia and precipitated fractionally by silver nitrate. The first three fractions consisted of microscopic needles containing respectively 53·25, 53·46, and 54·38 per cent. of silver. The last three fractions were composed of minute tabular crystals, containing 54·71, 54·78, and 55·12 per cent. of silver; silver butyrate contains 55·38 per cent. of silver. The last three fractions treated with a quantity of hot water insufficient to dissolve the whole, gave a solution which on cooling deposited pure silver isobutyrate. The other acid containing a larger percentage of carbon is regarded by Sigel as angelic acid, but neither caproic nor caprylic acid was detected. Old arnica root furnishes a distillate richer in acid than that obtained from the fresh root. Ten pounds of old root gave 12 grams of sodium salts, whilst 20 pounds of fresh root yielded only 10 grams.

The essential oil of arnica root is yellow, with a slight tinge of green and is quite neutral. Its sp. gr. = 0·975 at 16°, = 1·0087 at 0°. Arnica oil from the fresh root had a slightly greater sp. gr. The yield of oil is very variable; old roots gave 0·4 to 0·6 per cent., fresh roots, 1 per cent. The latter contained about 1 per cent. more carbon than the former. Submitted to fractional distillation the oil began to boil at 214°, the greater part passing over between 239° and 245°, the rest between 246° and 263°, leaving a brown resin. The several fractions, however, showed very little difference in composition. The oil was therefore boiled with alcoholic potash for some time, and the solution then diluted with water, which caused the separation of a lighter oily liquid. On neutralising the alkaline solution, a brown resinous substance was precipitated, from which ether extracted an oily body, and this submitted to distillation in a current of steam gave a yellowish liquid boiling at 224°–225°. Its sp. gr. at 12° was 1·015. It had the composition of phlorol, C¹¹H¹⁴O, and by treatment

with ethyl bromide in presence of potash, it gave ethyl-phlorol, a colourless liquid boiling between 215° and 217° .

The alkaline solution from which the phlorol had been obtained likewise furnished isobutyric acid.

The oily liquid which separated on addition of water to the alcoholic potash solution was submitted to fractional distillation, but could not be made to yield a definite product. It was therefore oxidised with a mixture of potassium chromate and sulphuric acid. Carbonic anhydride and a small quantity of a body having the characters of an aldehyde were produced, also acetic and some formic acid, besides a crystalline body melting at 45° – 46° , and having the properties and composition of thymoquinone. This portion of arnica oil must therefore contain some body nearly related to thymol. It could not, however, be thymol, because this portion of the oil was insoluble in potash; but when heated with strong hydriodic acid, it gave a considerable quantity of methyl iodide, and the residue furnished thymohydroquinone, together with a small quantity of phlorol, and resinous products.

Sigel has also examined the specimen of arnica oil, formerly the subject of Walz's experiments, with results precisely the same as those above detailed.

AROMATIC BODIES. See BENZENE DERIVATIVES.

ARRAGONITE. On the occurrence of Arragonite in the neighbourhood of Waltzsch in Bohemia, see APATITE (p. 116).

On Arragonite from Saebach, see Schrauf (*Jahrbuch f. Mineralogie*, 1873, 80).

ARSENIC. On crystals of Arsenic from Joachimsthal, see v. Zepharovich (*Jahrbuch f. Mineralogie*, 1875, 196).

Arsenic in Pyrites.—H. A. Smith (*Phil. Mag.* [4], xlv. 370; *Chem. News*, xxvi. 176) has determined the amount of arsenic in different kinds of pyrites, and its distribution during the manufacture of sulphuric acid therefrom, and in the several stages of the alkali manufacture. Reckoning the arsenic as arsenious oxide, the proportions found were:

Spanish pyrites: Thariss's	1.65 per cent. As_2O_3
" Massoull's	1.74 " "
Belgian " "	0.94 " "
Westphalian pyrites	1.88 " "
Norwegian " hard	1.65 " "
" soft	1.71 " "
Deposit in the flue leading from the pyrites kilns	
to the lead-chamber	46.86 " "
Deposit in the chamber	1.86 " "
Sulphuric acid	1.05 " "
Hydrochloric acid	0.69 " "
Sodium sulphate	0.03 " "
Soda-waste	0.44 " "
Sodium carbonate	none " "
Recovered sulphur by Mond's process	0.70 " "
After purification	none " "

Smith's observations further tend to show that some of the arsenic escapes into the air. When the salt used for the production of Hydrochloric acid is treated with sulphuric acid containing arsenic, the arsenic becomes converted into trichloride. This compound is said to be completely decomposed by contact with water, so that, after it has passed, together with hydrochloric acid gas, through the condensing towers it would scarcely be expected that any traces of arsenic originally present would be found in the escaping gas. This is, however, the case, a considerable quantity of the arsenic trichloride escaping the action of the water in the condensing towers, and passing together to the chimney. A deposit found in the flue leading from the salt-cake furnace to the condensing towers, the coke contained in the towers themselves, the gas in the flue leading to the chimney, and the smoke escaping from the chimney, were all found to contain arsenic.

	As_2O_3 per cent.
Flue deposit, mean of nine determinations	43.434
Coke from condensing towers, mean of three determinations	2.986

Air in the flue leading to the chimney, rate 31,722 cubic feet per hour, mean of twelve determinations:

	As_2O_3 in grains.
Per 1000 cubic feet	0.158
Per hour	5.012
Per day	115.134

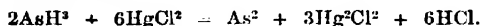
Air taken about 10 feet from bottom of chimney—

Mean of nine determinations per 1000 cubic feet	Grain. 0·086
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The arsenic probably escapes either as trioxide or trichloride; if as the latter, it is ultimately transformed into the former by the action of water vapour.

Arsenic in the Air of Rooms.—From experiments by H. Fleck (*Zeitschr. f. Biologie*, viii. 444) it appears that the air of rooms, the carpets or wall-papers of which are coloured with Schweinfurt green, often contains arsenetted hydrogen, produced by the action of moisture and organic matters on the arsenical pigment. The size, starch, paste, &c., used in hanging the paper appear to be especially active in this respect.

Detection.—Mayençon a. Bergeret (*Compt. rend. lxxix.* 118) adopt a method founded on the following reaction described by H. Rose :



Paper moistened with corrosive sublimate is exposed to the gas evolved from Marsh's apparatus. A trace of arsenic produces a lemon-yellow coloration, whilst a larger quantity gives a pale yellowish brown. Antimonetted hydrogen gives a dark grey coloration. One part of potassium arsenate in 120,000 of water may be thus detected. By the aid of this method it is found that arsenic is rapidly absorbed into the human system and passes at once into the urine.

In Sulphur.—Arsenic is sometimes tested for in sublimed sulphur and in flowers of sulphur, by boiling the suspected sulphur with ammonia, and then neutralising with hydrochloric acid. This method takes for granted that the arsenic exists in the sulphur as sulphide, or is converted into the sulphide by boiling with sulphur and ammonia. Arsenious acid, however, is the usual form in which arsenic occurs in sulphur, and it undergoes no change when boiled with aqueous ammonia. Sulphur-retted hydrogen must, therefore, be used for its detection (Hager, *Chem. Centr.* 1874, 376).

In Paper or Paperhangings.—A piece of the paper or paperhanging is moistened with a concentrated solution of sodium nitrate in a mixture of equal volumes of spirits of wine and water, and allowed to dry. The dry paper is then burnt on a flat porcelain plate, and usually smoulders without flame. The ashes are treated with water, to which are added a few drops of potash-solution to strong alkaline reaction, and the liquid is boiled and filtered. The filtrate acidified with sulphuric acid is treated with potassium permanganate so long as decoloration takes place on warming, a slight excess of the permanganate being finally added, leaving a faint red tint. The solution, if turbid, is filtered. After cooling and addition of more dilute sulphuric acid, a piece of pure zinc is introduced into the solution contained in a small flask fitted with a doubly perforated cork. In one perforation is fixed a piece of parchment dotted with silver nitrate solution, in the other a piece dotted with lead acetate. If arsenic be present, the silver paper is soon blackened. The lead paper serves as a check to show the absence of hydrogen sulphide. If the blackening does not occur, or if a slight blackening only, accompanied with a browning of the lead paper, ensues after some time, the absence of arsenic may be inferred (Hager, *Dingl. pol. J.* cevii. 511).

On the Detection of Arsenic in Toxicological Investigations, see Selmi (*Gazz. chim. ital.* ii. 544; *Chem. Soc. Jour.* 1873, 1165); also Kaiser (*Zeitschr. Anal. Chem.* xiv. 250; *Chem. Soc. Jour.* 1876, i. 754).

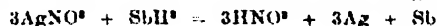
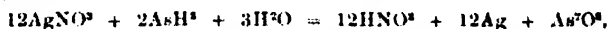
Estimation. 1. *By Precipitation as Ammonio-magnesium Arsenate.*—It is usually recommended to dry the precipitate at 100°–110°, at which temperature it is said to retain $\frac{1}{2}$ mol. water, so that its composition is represented by the formula $2(\text{NH}_4)\text{MgAsO}_4 + \text{H}_2\text{O}$. This mode of determination, however, is not exact, as the salt, when heated to the temperature above mentioned, gives off a little ammonia as well as water. For this reason, Rammelsberg (*Deut. Chem. Ges. Ber.* vii. 544) recommends that the precipitate be dried at 120° and then ignited, as first proposed by Levöl, whereby, if the calcination be conducted with the precautions recommended in H. Rose's *Traité de Chimie Analytique* (tome ii. 529), a residue will be obtained having the composition of magnesium pyro-arsenate, $\text{Mg}^2\text{As}_2\text{O}_7$. The dried precipitate is first heated for a long time to a temperature below 200°, then gradually raised to 300° or even 400°, and kept at that temperature for several hours, then heated to low redness, and finally to bright redness. When thus treated it gives off all its water and ammonia, without losing a trace of arsenic, whereas, if the salt be too quickly raised to a high temperature, a portion of the arsenic is reduced and volatilised, entailing considerable loss.

According to L. Wood (*Sill. Am. J.* [3], vi. 368) very exact results are obtained by precipitating the arsenic acid with a solution of magnesium chloride in alcohol of 85 per cent., containing 100 grams of salt per litre, and adding to the precipitated liquid, after twelve hours, half its own bulk of alcohol of the same strength. The precipitated arsenate of magnesium and ammonium is collected on a tared filter, washed with a mixture of 3 pts. water, 2 pts. alcohol, and 1 pt. ammonia, and dried, only that portion which cannot be easily detached from the filter being dried till of constant weight, while the greater portion is put into a porcelain crucible, some strong nitric acid added, the crucible covered, placed within a larger one, and heated till the weight becomes constant. The arsenic is calculated from the combined weights of $Mg^2As^2O^7$ and $2(NH^4MgAsO^4 + H^2O)$ found. To prevent the precipitation of magnesium arsenate, the precipitated ammonio-magnesium arsenate may be collected on a filter, dissolved in hydrochloric acid, reprecipitated by ammonia, and the alcohol added at once.

See also Macivor (*Chem. News*, xxii. 282; *Chem. Soc. Jour.* 1876, i. 756).

2. Rammelsberg also recommends the volumetric estimation of the acids of arsenic (arsenic acid being first reduced by sulphurous acid) by supersaturation with potassium carbonate, and addition of starch-paste and a normal solution of iodine. In applying this method, however, to the estimation of arsenic in ignited magnesium pyroarsenate, he finds that the results often come out too low.

3. *Volumetric estimation of small quantities of Arsenic and Antimony.*—The precipitation of silver nitrate by the trihydrides of arsenic and antimony, according to the equations:



may be utilised for the estimation of small quantities of these metals.

The gas generated in Marsh's apparatus is passed into a measured volume of silver solution of known strength, and when the precipitation is complete, the excess of silver in the solution is estimated by means of a standard solution of sodium chloride.

The difference gives the quantity of silver precipitated by the arsenetted or antimonetted hydrogen, and thence the quantity of arsenic or antimony present may be calculated: $Ag = 0.11574$ $As = 0.3765$ Sb .

The quantities of arsenic and antimony in a mixture may be found by determining (1) The total quantity of silver precipitated; (2) By titration of the arsenious acid, whereby the quantity of silver precipitated by the arsenetted hydrogen becomes known; (3) By difference, the amount of silver precipitated by the antimonetted hydrogen, whence the quantity of antimony present may be calculated (Houzeau, *Compt. rend.* lxxv. 1823).

4. For the complete separation of arsenic from animal matters, and its estimation in various tissues, the following method is recommended by Gautier (*Compt. rend.* lxxxi. 239). 100 grams of the mashed tissue are gently warmed with 30 grams of strong nitric acid. When the liquefied mass becomes viscous and tends to adhere to the sides of the vessel, it is removed from the source of heat, to avoid deflagration, which would be attended with loss of arsenic. Six grams of sulphuric acid are then added, and the mixture is warmed until the acid emits fumes, when 15 grams of nitric acid are introduced, drop by drop. The whole reliquefies, emits nitrous fumes, and leaves a carbonaceous residue which is easily pulverised, and exhausted with boiling water. The cherry-coloured filtrate contains all the arsenic, but no nitric compounds detectable by ferrous sulphate. To the warmed liquid a few drops of sodium bisulphite are added, and the arsenic is precipitated by sulphuretted hydrogen.

Experiment shows that no arsenic is lost by the first treatment with nitric acid, even though small quantities of chlorides may be present. The powerful oxidation induced on the addition of the sulphuric acid is never accompanied by deflagration, and the final addition of nitric acid prevents the reduction of the sulphuric acid. The residuary charcoal yields a scarcely visible trace of arsenic in Marsh's apparatus.

5. For the determination of very small quantities of arsenic either in mineral or in organic substances, Cronkhydis (*Bull. Soc. Chim.* [2], xxv. 348) gives the preference to the method, first proposed by Gautier, of evolving the arsenic from a Marsh's apparatus in the form of arseniuretted hydrogen, and weighing the metallic arsenic obtained in the combustion-tube. As evidence of the extreme accuracy of this method, the following results are given:—

Orpiment of absolute purity was taken:—

Wt. of orpiment.	Metallic arsenic found.	Metallic arsenic calculated.
0.0108	0.0065	0.00658
0.0052	0.0030	0.00308

On determining the arsenic in a portion of the same sample of orpiment by the ammonium-magnesium arsenate method, inaccurate results were obtained, as will be seen from the following—

Orpiment taken.	Ammonium-magnesium arsenate obtained.	Arsenic found.	Arsenic calculated.
0.55	0.8755	0.344	0.3353

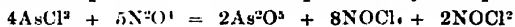
Gautier's method is equally accurate when applied to the determination of arsenic contained in large quantities of organic matter. Known volumes of a standard orpiment solution (0.5 gram of orpiment dissolved in 1 litre of water) were introduced into 100 grams of meat, and the amount of arsenic determined. The results are given below—

Wt. of meat taken.	c.c. of solution taken.	Wt. of orpiment.	Wt. of arsenic obtained.	Arsenic calculated.
100 grams.	5	0.0025	0.0015	0.00152
" "	10	0.0050	0.0030	0.00301
" "	5	0.0025	0.0015	0.00152

The carbonisation of the organic matter must not however be carried too far, as it is found that the greater part of the arsenic then remains in the charcoal as sulphide. In order to be quite certain that all the arsenic is in solution, the organic matter which has been successively treated with nitric acid, sulphuric acid, and again with nitric acid, is calcined, and the residue treated again but not calcined. By this process all the arsenic is obtained, and no sulphide remains in the charcoal.

6. For the detection of arsenic in wines (introduced together with fuchsin as colouring matter), the following process is given by C. Husson (*Compt. rend.* lxxxiii. 199). When arsenetted hydrogen is passed into a solution of iodine in benzene, the colour of that solution is rapidly destroyed, whereas it is not affected by pure hydrogen. This reaction is applied as follows. The evaporated residue of the wine having been treated by the ordinary processes, so as to obtain the arsenic in the form of a potassium salt, this salt is dissolved in distilled water, and the solution divided into two parts. One of these is reserved for qualitative examination, and the other is divided into two parts, in one of which the arsenic is approximately determined by pouring the liquid into a Marsh's apparatus which is evolving pure hydrogen, and passing the gas into a measured quantity of a standard solution of iodine in benzene, and as this is decolorised, gradually adding more from a burette until the decolorisation ceases. In the other part of the solution the quantity of arsenic is exactly determined by pouring it into a Marsh's apparatus as before, and allowing the evolved gas to pass through a series of about six test-tubes, each containing a known amount of iodine: for example, in the 1st 0.01 gram; 2nd and 3rd, 0.005 gram; 4th, 0.001 gram; 5th, 0.0005 gram; and 6th, 0.0001; but these quantities may be varied according to the indications afforded by the previous experiment. By noting the number of test-tubes coloured, the exact quantity of arsenic introduced into the Marsh's apparatus can be ascertained.

Arsenious Chloride, AsCl₃. When nitrogen tetroxide is distilled into arsenious chloride, a liquid is formed which floats on the chloride, together with solid arsenic oxide, which remains at the surface of contact of the two liquids, and is produced in larger quantity on mixing them, and leaving the whole for some time at a temperature about 0°. The liquid contains oxychlorides of nitrogen, and the reaction appears to take place in the manner represented by the equation:



(Geuther, *J. pr. Chem.* [2], viii. 354).

Arsenious Fluoride, AsF₃. This compound is best prepared by heating together 4 parts of arsenic trioxide, 5 of calcium fluoride, and 12 of phosphoric hydrogen sulphate, H₂SO₄ (obtained by adding sulphuric oxide or the Nordhausen acid in due proportion to common oil of vitriol). It is also formed by heating sodium or ammonium fluoride (preferably the latter) with arsenious bromide or chloride. When perfectly anhydrous it does not act on glass. It is miscible with alcohol and ether. It boils at a little above 60°, and its vapour-density (determined in Hofmann's apparatus) is 4.3 (calc. for 2 vols. = 4.6). It absorbs dry ammonia gas in large quantity, producing a white non-crystalline mass, which dissolves in alcohol and ether, but is decomposed by water, yielding fluoride and arsenite of ammonium. With phosphorous bromide or chloride it yields phosphorous fluoride, PF₃ (q. v.), and arsenious bromide or chloride (Macivor, *Chem. News.* xxx. 169).

Arsenious Hydride, or Arsine, AsH₃. This gas is decomposed by strong sulphuric or hydrochloric acid, with deposition of brown flocks consisting, not of a solid arsenide of hydrogen, As²H₂, as commonly supposed, but of metallic arsenic, a

small quantity of sulphur dioxide being formed at the same time. With *arsenious chloride* arsenetted hydrogen forms hydrochloric acid and metallic arsenic,



This explains why metallic arsenic is attacked with difficulty by hydrochloric acid gas, and scarcely at all by the aqueous acid. *Phosphorous chloride* acts in a similar manner, forming hydrochloric acid and a phosphide of arsenic,



(Janowsky, *Deut. Chem. Ges. Ber.* 1873, 216).

With regard to the solid arsenide of hydrogen, said to be deposited when metallic arsenides are dissolved in acids, Janowsky finds that it consists in almost all cases of metallic arsenic; the arsenides of potassium and sodium, however, when decomposed by water, leave a brown velvety residue of solid hydrogen arsenide, AsH .

Engel (*Compt. rend.* lxxvii. 1545) also finds that the solid residue left on dissolving arsenide of zinc in hydrochloric acid consists of finely divided arsenic; so likewise does the brown substance formed by the action of hypophosphorous acid on arsenic oxide dissolved in hydrochloric acid. When arsine is passed over sulphur in sunlight, sulphide of arsenic is formed, and hydrogen sulphide is liberated, but immediately decomposed by the excess of arsenic, the tube becoming covered with an iridescent film of arsenious sulphide (F. Jones, *Chem. Soc. J.* 1876, i. 648).

Arsenious and Arsenic Oxides and Acids. 1. *Heat of Formation and Solution* (J. Thomsen, *Deut. Chem. Ges. Ber.* vii. 1002).—The following determinations, made by processes differing from those employed by Favre in 1853, show, nevertheless, a very close agreement. The heat of solution of *amorphous* As_2O_3 in water was ascertained by observing the difference in the heats evolved when powdered arsenious oxide and its solution were respectively added to an excess of sodium hydrate. The result, $(\text{As}_2\text{O}_3, \text{Aq}) = -7550$, indicates that the anhydride dissolves *as such* in water, no hydrates being formed. The two hydrates of arsenic acid, $\text{H}^1\text{As}^1\text{O}^1$ and $\text{H}^2\text{As}^1\text{O}^1$, were examined. The solution of the hydrate $\text{H}^1\text{As}^1\text{O}^1$ lowers the temperature from 18° to 2° , but, as it almost immediately begins to combine with water, the temperature quickly rises again to 30° , and if only the requisite quantity of water has been used, the whole solidifies to a mass of the hydrate $\text{H}^2\text{As}^1\text{O}^1$. The oxidation of arsenious to arsenic acid was performed with iodine, keeping the arsenious acid in excess. Metallic arsenic was oxidised with bromine-water.

The following are the results for one molecule of the respective compounds, at 18° :

Heat of solution	$(\text{As}_2\text{O}_3, \text{Aq})$	-7550	gram-degrees.
	$(\text{As}_2\text{O}_3, \text{Aq})$	$+6000$	"
	$(\text{H}^1\text{As}^1\text{O}^1, \text{Aq})$	-400	"
	$(\text{H}^2\text{As}^1\text{O}^1, \text{Aq})$	$+1300$	"
Formation of hydrates	$(\text{As}_2\text{O}_3, 2\text{H}_2\text{O})$	-4710	"
	$(\text{As}_2\text{O}_3, 3\text{H}_2\text{O})$	-6800	"
Formation of the anhydrides	(As_2O_3)	-152590	"
	(As_2O_3)	-219100	"
Formation of the acids in aqueous solution	$(\text{As}_2\text{O}_3, \text{Aq})$	-147040	"
	$(\text{As}_2\text{O}_3, \text{Aq})$	-225400	"
	$(\text{H}^1\text{As}^1\text{O}^1, \text{Aq})$	-215240	"
	$(\text{As}_2\text{O}_3, \text{Aq}, \text{O})$	-78350	"

Neutralisation-phenomena and Basicity of Arsenious Acid in Aqueous Solution (Thomsen, *ibid.* 935).—The analogy existing between arsenic and phosphoric acids does not extend to arsenious and phosphorous acids. The composition of the phosphites shows that phosphorous acid is bibasic, and the neutralisation-phenomena of this acid distinctly prove the bibasic character of the molecule PO_2H_2 . (See PHOSPHORUS.)

The arsenites, on the contrary, differ in constitution from the phosphites, and the neutralisation-phenomena of arsenious acid show that the molecule As_2O_3 in aqueous solution forms a bibasic acid, while a hydrate, AsO_2H^1 , analogous in composition to phosphorous acid, if it has any existence, must be regarded as a monobasic acid.

An aqueous solution of arsenious acid, having a concentration represented by the formula $\text{As}_2\text{O}_3 + 400 \text{H}_2\text{O}$, was mixed with a solution of sodium hydrate in the proportions of 1 mol. of As_2O_3 to 1, 2, 4 and 6 mols. of NaOH . The *mola*-solution contained in the several experiments, 400, 200, and 100 mols. of water for each molecule of sodium hydrate. The evolution of heat in these experiments was as follows:—

<i>a</i>	$\text{As}^2\text{O}^3\text{Aq. aNaOHAq.}$
1	7300 heat-units.
2	13780 "
4	15070 "
6	15580 "

These numbers show, in the first place, that arsenious acid is a weak acid: for the heat of neutralisation amounts to only half of that of phosphorous acid (28370), hydrochloric acid (27480), and the majority of the acids which have been investigated; an aqueous solution of even carbonic acid, boric acid, hypochlorous acid, or sulphuretted hydrogen possesses a greater heat of neutralisation than arsenious acid. The numbers show further that the molecule As^2O^3 saturates only 2 mols. of sodium hydrate, the evolution of heat on neutralisation of As^2O^3 being—

For the first molecule of NaOH,	7300	} 15580 heat-units.
" second "	6480	
" third and fourth "	2.890	
" fifth and sixth "	2.250	

The strong evolution of heat ceases with the second molecule of sodium hydrate. The heat of neutralisation of phosphorous acid is quite different. If for the sake of comparison it is calculated for 2 mols. of PO^3H^3 or $\text{P}^2\text{O}^3\text{Aq.}$ it is—

For the first molecule of NaOH,	14860	} 57880 heat-units.
" second "	14810	
" third and fourth "	2.13536	
" fifth and sixth "	2.572	

The evolution of heat in this case is proportional to the amount of soda, till the latter reaches 4 mols., so that the simple molecule PO^3H^3 is bibasic. Experiments on neutralisation with baryta gave similar results. An aqueous solution of arsenious acid, $\text{As}^2\text{O}^3\text{Aq.}$ gives—

With 1 mol. of $\text{BaO}^2\text{H}^2\text{Aq.}$	14020 heat-units
" 2 " "	15620 "

This shows, in the first place, that the law according to which all soluble bases produce about the same heat of neutralisation with the same acids, holds good for arsenious acid: for 2 mols. of sodium hydrate give 13780 heat-units, while 1 mol. of barium hydrate gives 14020; further, that the neutralisation is completed with 1 mol. of barium hydrate: for the second molecule gives only 1600 units as the amount of heat.

Arsenious oxide, therefore, in aqueous solution, acts as a weak bibasic acid, and its salts, when they contain a larger amount of base, are basic salts.

Arsenious acid and hydrochloric acid, mixed together in aqueous solution, produce no thermic reaction: for the evolution of heat with As^2O^3 to 4HCl amounts to only 160 units.

Solubility of Arsenious Oxide in Water.—L. A. Buchner (*N. Rep. Pharm.* xxii. 285) has examined the solubility in water of the two modifications of arsenious oxide; 1 part of the crystallised oxide dissolves in about 355 parts of water at 25° , after a few days' contact; 1 part of the amorphous acid, similarly treated, requires only 108 parts of water to dissolve it; 1 part of the crystallised acid dissolves in 46 parts of water, when the solution is prepared at the boiling heat and then left for twenty-four hours at 15° ; 1 part of the amorphous acid, similarly treated, dissolves in 30 parts of water.

Action of Iodine on Arsenious Acid.—According to Zinno (*N. Rep. Pharm.* xxii. 385), when iodine suspended in water is added to a boiling solution of arsenious acid till a permanent coloration is produced, and the liquid, after filtration through charcoal powder, is evaporated till it begins to become coloured and opaque, and then left for some days in a cool place, shining crystals are deposited, having the composition $\text{As}^2\text{O}^3\text{I}^4$, that is to say, arsenic oxide in which 2 at. oxygen are replaced by 4 at. iodine. This iodarsenic oxide is more soluble in water than vitreous arsenic oxide; soluble also in alcohol, insoluble in ether, and in benzene. It is decomposed by air, by light, and by prolonged boiling of its aqueous solution, yielding arsenic and hydriodic acids. The undecomposed aqueous solution exhibits the reactions of a soluble iodide. On pouring a solution of potassium iodide into a hot incomplete solution of iodarsenic acid, potassium iodarsenate, $\text{As}^2\text{O}^3\text{I}^4.2\text{KI}$, separates in fine silvery scales. The corresponding ammonium salt, obtained by neutralisation, is a colourless crystalline mass.

According to Wegner, on the other hand (*Liebig's Annalen*, clxxiv. 129), the supposed iodarsenic acid has no existence, the crystals obtained by Zinno's process con-

sisting merely of arsenious oxide containing a trace of hydriodic acid. When iodine is dissolved in a hot solution of arsenious acid, the latter is oxidised, with formation of arsenic and hydriodic acids, which act on each other again when the solution is concentrated, free iodine and arsenious acid being reproduced.

Arsenates.—When the arsenates of barium and lead are boiled with nitric acid of variable concentration, and the solutions left to cool, decomposition takes place, and crystals of barium or lead nitrate are deposited, provided the nitric acid is sufficiently concentrated to render the nitrates of lead and barium insoluble in the liquid. If water be added to a solution of barium arsenate in nitric acid, it remains clear; but if a boiling solution of lead arsenate in nitric acid be diluted with water, it quickly deposits needles of biphumbic arsenate.

The phosphates of lead and barium react with nitric acid in a precisely similar manner (Duvillier, *Compt. rend.* lxxi. 1251).

On the Compounds of Arsenic acid with Molybdic acid, see MOLYBDENUM.

Sulphides. The experiments of Nilsson, already described (2nd Suppl. 106), have been continued (*J. pr. Chem.* [2], xii. 295; xiii. 1), chiefly with the view of determining the conditions under which realgar and orpiment are produced.

1. **Arsenic disulphide, As_2S_3 .** *Realgar.*—Arsenious anhydride and sulphur heated together, according to Berzelius's directions, in the proportion of $2As_2O_3$ to $7S$, yielded a transparent ruby-red glass containing 42.94 per cent. of sulphur, or rather more than enough for As_2S_3 . On mixing it with the theoretical quantity of arsenious anhydride, and again distilling, a distillate was obtained, having the same appearance, and still containing too much sulphur for realgar, nearly enough, in fact, for orpiment; and even after this treatment had been repeated several times, the sulphur never fell below 38 per cent., whereas realgar contains 20.01. A better result was obtained by heating 3.95 grams of arsenious oxide and 2.34 grams of finely-powdered sulphur for about seven hours in a stream of carbonic anhydride. The mass then slowly changed into a cinnabar-coloured crystalline substance, having the composition As_2S_3 , and dissolving partially in caustic potash with a black residue, which reaction is characteristic of realgar.

During the preparation, a little metallic arsenic was liberated, and it was found by a special experiment, that an oxide and a sulphide of arsenic act on one another like the corresponding lead compounds, that is to say, with reduction of arsenic and formation of sulphurous oxide.

An opaque amorphous glassy substance, formed on heating arsenious oxide and sulphide together, was found to contain 25.43 per cent. sulphur and 72.10 arsenic, the proportion of arsenic being larger than in the disulphide. This result confirms Hausmann's hypothesis, that a small admixture of arsenious oxide renders realgar uncrystallisable. The ruby-red glass obtained as a product of the first-mentioned distillations consists of a mixture of disulphide and trisulphide of arsenic.

If hydrogen be substituted for carbonic anhydride in expelling air from the retort in which the distillation is performed, the sulphide of arsenic is reduced to metal, with evolution of sulphuretted hydrogen. The higher sulphide is not so easily reduced as the disulphide. Sodium sulpharsenate is also reduced to metallic arsenic (contrary to Rose's assertion) by heating in an atmosphere of hydrogen.

After expelling the oxygen from the arsenic disulphide by heating in an atmosphere of hydrogen, and adding a quantity equal to that which was thereby removed, pure realgar was obtained by fusing the mixture in an atmosphere of carbonic anhydride.

Sourmont states that realgar is formed when arsenic trisulphide is heated in a sealed tube with sodium bicarbonate; H. Rose, on the other hand, asserts that arsenic is volatilised, and sulpharsenate remains. Rose's experiments were repeated by Nilsson, and his statement confirmed.

Berzelius obtained a 'hyposulpharsenite' as a bulky brown precipitate, by dissolving arsenic trisulphide in sodium carbonate, and letting the solution cool. In repeating this experiment with a strong boiling solution of sodium carbonate, Nilsson observed the precipitation of a heavy crystalline powder, while sulphuretted hydrogen was evolved. This powder melts, forming a red liquid, which assumes a crystalline form on cooling. After being dried over sulphuric acid, it loses no weight at 100° . It forms a yellow solution with caustic potash, and a purple solution in caustic soda, which soon becomes clear, while a black precipitate falls. The solution contains an arsenite and a sulpharsenite. Analysis proved the crystalline powder to be pure arsenic disulphide.

The most characteristic test for realgar is the precipitate which settles from its solution in alkaline hydrates; this substance was regarded by Berzelius as As_2S_3 , and by Kühn as arsenic contaminated with arsenic disulphide. Kühn accounts for

its formation by the reaction $3\text{As}^2\text{S}^2 = 2\text{As}^2\text{S}^3 + \text{As}^2$, which requires that the liberated arsenic should form 23·36 per cent. of the realgar used.

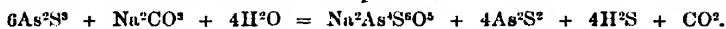
Various experiments made by Nilsson show that this reaction really takes place, but that the arsenic acts on the excess of alkaline hydrate on prolonged boiling. No arsenetted hydrogen is liberated, but probably hydrogen, owing to the decomposition of water by the finely-divided arsenic. The whole of the arsenic disulphide is not decomposed by boiling with caustic alkali, for the arsenic encrusts it, and prevents its action. This accounts for the sulphur found by Berzelius, and satisfactorily disproves the existence of the compound As^{12}S .

Realgar on exposure to air becomes partially oxidised; and the liberated sulphur combines with the arsenic to form trisulphide. This was demonstrated by dissolving the arsenious oxide and sulphide, encrusting some realgar which had been exposed to air, in alkaline carbonate; the trisulphide was precipitated from the solution by addition of hydrochloric acid, and the arsenious acid was recognised in the filtrate by the reaction with sulphuretted hydrogen. This oxidation occurs in nature. Orpiment is probably a secondary product, formed by the action of air on realgar, and arsenious anhydride invariably accompanies orpiment.

Rose states that arsenic disulphide melts in a current of chlorine, to a yellowish-brown liquid, which becomes brown by absorption of chlorine, and has the composition $\text{AsCl}^2\cdot 3\text{SCL}$. Nilsson, after fractionating the product obtained in this manner, found it to consist of a mixture of sulphur chloride and arsenious trichloride. Chlorine acts on trisulphide of arsenic less energetically than on the disulphide, but the products obtained are the same.

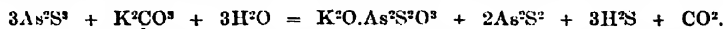
2. *Arsenic Trisulphide*.—When arsenic trisulphide is added to a concentrated boiling solution of sodium and potassium carbonate, arsenic disulphide is precipitated, and the remaining solution deposits a bulky brown precipitate of sodium trisulpharsenite, $\text{NaAs}^2\text{S}^3 + 4\text{H}^2\text{O}$ or $\text{Na}^2\text{S}\cdot 3\text{As}^2\text{S}^3 + 8\text{H}^2\text{O}$, which is decomposed by water.

When, instead of allowing the solution of arsenic trisulphide in sodium carbonate to cool, it is kept for a long time at 70° – 80° , a yellowish-brown crust is deposited, consisting of slightly impure arsenic trisulphide. When the above-mentioned solution, after removal of arsenic disulphide, is evaporated till it solidifies on cooling, an amorphous brown mass is obtained, which, on standing, deposits four different crystalline substances, viz. (1) Disodic oxysulpharsenate, $\text{Na}^2\text{As}^2\text{S}^2\text{O}^3 + 7\text{H}^2\text{O}$ or $2\text{Na}^2\text{O}\cdot 2\text{As}^2\text{S}^2\text{O}^3 + 7\text{H}^2\text{O}$, in garnet-red hexagonal crystals (sometimes short prisms), sparingly soluble in water, more soluble in alkaline liquids, and decomposed by hydrochloric acid, leaving a yellow residue; (2) Trisodic sulpharsenate, $2\text{Na}^2\text{As}^2\text{S}^3 + 15\text{H}^2\text{O}$, or $3\text{Na}^2\text{S}\cdot \text{As}^2\text{S}^3 + 15\text{H}^2\text{O}$, in well-formed monoclinic prisms, easily soluble in water, and decomposed by hydrochloric acid, with separation of As^2S^3 and sulphur; (3) Sodium bicarbonate in small white crystals; (4) Disodic arsenate, $\text{Na}^2\text{HAsO}^4 + 7\text{H}^2\text{O}$, or $2\text{Na}^2\text{O}\cdot \text{H}^2\text{O}\cdot \text{As}^2\text{O}^3 + 14\text{H}^2\text{O}$, in colourless crystals easily soluble in water, and not decomposed by hydrochloric acid. The following reactions account for the formation of these several products:—



The sodium arsenite is converted into arsenate, either by decomposition of water or by the oxidising action of the air.

The products formed by boiling arsenic trisulphide with potassium carbonate are similar to those obtained with sodium carbonate, excepting that, instead of a disoxysulpharsenate, a trioxysulpharsenate of potassium, $\text{K}^2\text{O}\cdot \text{As}^2\text{S}^2\text{O}^3 + 2\text{H}^2\text{O}$, is produced:



Sulpharsenites.—When an alkaline or earthy hydrosulphide is saturated at ordinary temperatures with arsenic trisulphide, salts are produced having the composition As^2SR or $\text{R}^2\text{S}\cdot \text{As}^2\text{S}^3$; of these, however, only the calcium salt, $\text{CaS}\cdot \text{As}^2\text{S}^3 + 10\text{H}^2\text{O}$, has been obtained in the crystalline state. They are decomposed by water, with formation of insoluble acid compounds, such as $\text{Na}^2\text{S}\cdot 2\text{As}^2\text{S}^3 + 6\text{H}^2\text{O}$, &c. On boiling the solution of potassium sulpharsenite, $\text{K}^2\text{S}\cdot \text{As}^2\text{S}^3 + 5\text{H}^2\text{O}$, a crystallised acid sulpharsenite, $\text{K}^2\text{S}\cdot 3\text{As}^2\text{S}^3 + 2\text{H}^2\text{O}$, is formed, with evolution of hydrogen sulphide. This, like the other acid sulpharsenites, is decomposed very slowly, or incompletely, by hydrochloric acid. In a vacuum more basic salts may be formed, such as $2\text{R}^2\text{S}\cdot \text{As}^2\text{S}^3$ and $3\text{R}^2\text{S}\cdot \text{As}^2\text{S}^3$. This, however, is not the case with the sulphides of the alkali-metals, which, when more than 1 mol. As^2S^3 is present to 1 mol. R^2S , yield a sulpharsenate and free arsenic. Ammonium hydrosulphide forms, under all circumstances, only one compound, viz., $(\text{NH}^4)^2\text{S}\cdot \text{As}^2\text{S}^3 + 4\text{H}^2\text{O}$. From a solution of calcium sulpharsenite, $3\text{CaS}\cdot \text{As}^2\text{S}^3$, a basic salt, $7\text{CaS}\cdot \text{As}^2\text{S}^3 + 25\text{H}^2\text{O}$, or $\text{Ca}^3\text{As}^2\text{S}^3\cdot 4\text{CaS} + 25\text{H}^2\text{O}$, may be obtained in fine crystals,

reas the solutions of corresponding barium and strontium sulpharsenites deposit salts of the salts $\text{R}^2\text{As}^2\text{S}^3 + 15\text{H}^2\text{O}$ or $2\text{R}^2\text{S}.\text{As}^2\text{S}^3 + 15\text{H}^2\text{O}$.

3. *Arsenic Pentasulphide*, As^2S^5 .—The precipitate formed by hydrochloric in a solution of a sulpharsenate at ordinary temperatures consists of the hydrosulphide, AsS^2H^3 or $3\text{H}^2\text{S}.\text{As}^2\text{S}^3$, which does not give up the whole of its hydrogen sulphide till after prolonged boiling with excess of hydrochloric acid. The pentasulphide thus formed contains water, and when dried over sulphuric acid has the composition $\text{As}^2\text{S}^5 + \text{H}^2\text{O}$. When dried in the air it undergoes partial oxidation, with nation of arsenious oxide and separation of sulphur. In consequence of this action, arsenic pentasulphide precipitated in the cold and air-dried always contains sulphur; and herein may be found an explanation of the observation made by Kiger (1st Suppl. 226), that ammonium thiosulphate is formed on treating the pentasulphide with ammonia; also of the fact, observed by Berzelius, that when the pentasulphide is dissolved in alkaline hydrosulphides, a small quantity of sulphur remains undissolved. The tendency of the pentasulphide to split up into trisulphide and free sulphur is seen in its behaviour towards silver solution, the product thereby being arsenious acid unmixt with arsenic acid. The separation of sulphur which takes place when the pentasulphide is dissolved in potassium arsenate likewise indicates the comparatively loose attachment of two-fifths of the sulphur contained in it.

When hydrosulphides are saturated with arsenic pentasulphide, the formation of normal salts AsS^2R^2 or $3\text{R}^2\text{S}.\text{As}^2\text{S}^3$ appears to be the exception, the more ordinary products being salts of the forms $5\text{R}^2\text{S}.\text{As}^2\text{S}^3$ and $6\text{R}^2\text{S}.\text{As}^2\text{S}^3$, or else the double salts, $3\text{R}^2\text{S}.\text{As}^2\text{S}^3 + 2\text{R}^2\text{S}.\text{As}^2\text{S}^3 + 8\text{H}^2\text{O}$.

The following sulphur-salts of arsenic have been examined by Nilsson:—

$\text{K}^2\text{S}.\text{As}^2\text{S}^3 + 5\text{H}^2\text{O}$	Amorphous bright-red salt.
$3\text{K}^2\text{S}.\text{As}^2\text{S}^3 + 8\text{H}^2\text{O}$	Blood-red amorphous mass.
$\text{K}^2\text{S}.\text{As}^2\text{S}^3 + 2\text{H}^2\text{O}$	Red-brown, microscopic crystals.
$3\text{K}^2\text{S}.\text{As}^2\text{S}^3 + 2\text{H}^2\text{O}$	Long, four-sided, deliquescent prisms.
$\text{K}^2\text{O}.\text{As}^2\text{S}^3 + 2\text{H}^2\text{O}$	Small colourless pointed crystals.
$\text{Na}^2\text{S}.\text{As}^2\text{S}^3 + \text{H}^2\text{O}$	Dingy-brown, amorphous salt.
$\text{Na}^2\text{S}.\text{As}^2\text{S}^3 + 6\text{H}^2\text{O}$	Red-brown, amorphous.
$\text{Na}^2\text{S}.\text{As}^2\text{S}^3 + 8\text{H}^2\text{O}$	Amorphous kermes-like body.
$3\text{Na}^2\text{S}.\text{As}^2\text{S}^3 + 16\text{H}^2\text{O}$	Large yellow monoclinic prisms.
$3\text{Na}^2\text{S}.\text{As}^2\text{S}^3 + 18\text{H}^2\text{O}$	Small, short, opaque rhombic octohedrons.
$\text{Na}^2\text{O}.\text{As}^2\text{S}^3 + 7\text{H}^2\text{O}$	Fine garnet-red crystals.
$(\text{NH}^4)^2\text{S}.\text{As}^2\text{S}^3 + 4\text{H}^2\text{O}$	Red crystalline salt.
$6(\text{NH}^4)^2\text{S}.\text{As}^2\text{S}^3$	Yellow, amorphous, shining mass.
$\text{BaS}.\text{As}^2\text{S}^3$	
$\text{BaS}.\text{As}^2\text{S}^3 + 2\text{H}^2\text{O}$	Brown shining mass.
$\text{BaS}.\text{As}^2\text{S}^3 + x\text{H}^2\text{O}$	Green mass.
$2\text{BaS}.\text{As}^2\text{S}^3 + 5\text{H}^2\text{O}$	Greyish-green.
$2\text{BaS}.\text{As}^2\text{S}^3 + 5\text{H}^2\text{O}$	Indigo-blue.
$2\text{BaS}.\text{As}^2\text{S}^3 + 15\text{H}^2\text{O}$	Large monoclinic prisms, with diamond lustre.
$5\text{BaS}.\text{As}^2\text{S}^3 + 6\text{H}^2\text{O} (?)$	Needle-shaped microscopic crystals.
$3\text{BaS}.\text{As}^2\text{S}^3 + 14\text{H}^2\text{O}$	Yellowish, flat, pointed prisms.
$3\text{BaS}.\text{As}^2\text{S}^3 + 2\text{BaS}.\text{As}^2\text{S}^3 + 8\text{H}^2\text{O}$	Yellowish prisms, with diamond lustre.
$2(\text{SrS}.\text{As}^2\text{S}^3) + 5\text{H}^2\text{O}$	Amorphous, orange-yellow mass.
$2\text{SrS}.\text{As}^2\text{S}^3 + 15\text{H}^2\text{O}$	Large monoclinic crystals.
$3\text{SrS}.\text{As}^2\text{S}^3 + 2\text{SrS}.\text{As}^2\text{S}^3 + 8\text{H}^2\text{O}$	Yellow radio-crystalline mass.
$\text{CaS}.\text{As}^2\text{S}^3 + 10\text{H}^2\text{O} (?)$	Long slender prisms with silky lustre.
$\text{CaS}.\text{As}^2\text{S}^3 + 10\text{H}^2\text{O}$	Brown, amorphous.
$\text{CaS}.\text{As}^2\text{S}^3 + 10\text{H}^2\text{O}$	The same.
$7\text{CaS}.\text{As}^2\text{S}^3 + 25\text{H}^2\text{O}$	Long, flexible, white, nacreous, four-sided prisms.
$5\text{CaS}.\text{As}^2\text{S}^3 + 12\text{H}^2\text{O}$	Radio-crystalline, easily soluble mass.
$3\text{CaS}.\text{As}^2\text{S}^3 + 20\text{H}^2\text{O}$	Yellowish rhombohedrons.
$\text{MgS}.\text{As}^2\text{S}^3 + 5\text{H}^2\text{O}$	Brown mass.
$2\text{MgS}.\text{As}^2\text{S}^3 + 8\text{H}^2\text{O}$	soluble salt. It.
$3\text{MgS}.\text{As}^2\text{S}^3 + 9\text{H}^2\text{O}$	
$5\text{MgS}.\text{As}^2\text{S}^3 + 30\text{H}^2\text{O}$	

Dibario Sulpharsenit, $2\text{BaS}.\text{As}^2\text{S}^3 + 5\text{H}^2\text{O}$, separates from its solution, on evaporation in a vacuum, as a greyish-green precipitate, which, if left for some time in the mother-liquor, turns indigo-blue without change of composition, and retains this colour even after washing with water.

ARSENIOSIDERITE. This mineral occurs in a bed of manganese ore at Romanèche Macon (Seine et Loire), and is generally mixed with particles of wax. A remarkably pure specimen, in fibrous crystals, of sp. gr. 3.36 and hardness 1.5, gave, after separation of a few particles of black manganese, the following analytical results:—

	As ² O ³ .	Fe ² O ³ .	CaO.	MgO.	K ² O.	H ² O.
(1.)	39.90	35.83	15.57	—	—	8.70 = 100
(2.)	39.83	35.67	15.98	0.18	0.47	7.87 = 100.

The water in these analyses was estimated by difference: a direct determination gave 8.21 per cent. The results agree approximately with the formula

$5\text{CaO} \left\{ \begin{array}{l} \text{H}^2\text{O} \\ \text{Fe}^2\text{O}^3 \end{array} \right\} 3\text{As}^2\text{O}^3 + 3(\text{Fe}^2\text{O}^3.2\text{H}^2\text{O})$. The latter member, which is known as a distinct species named *Xanthosiderite*, exhibits a marked resemblance to arseniosiderite in its physical characters (Church, *Chem. Soc. Jour.* [2], xi. 102).

ARSENPHENYL CHLORIDE. See PHENYL COMPOUNDS.

ARSINE, AsH³. See p. 124.

ASPARAGINE, C⁴H⁸N²O³. *Supposed Transformation of the Asparagine of Leguminosæ into an Albuminoid.*—The researches of Piria and Pasteur, though contradictory in some respects, nevertheless agree, together with those of other authors, in showing that asparagine is always formed during the germination of leguminous plants, whether in light or in darkness, and that as the vegetation advances, this substance is transformed into an albuminoid if the plant grows in the dark, and remains unaltered if it grows in the light (2nd Suppl. 108). These statements respecting the alteration of the asparagine, appear, however, to rest on a very slender experimental basis, and according to Mercadante they are altogether incorrect. From experiments on the yellow lupine (*Lupinus luteus*) and the kidney-bean (*Phaseolus vulgaris*), he finds that the asparagine formed during the germination of the plant is, during the subsequent growth, whether in the dark or in the light, invariably more or less transformed into aspartic and succinic acids and ammonia, without a trace of albuminous substance. The transformation is accelerated by exposure to light, the products of the decomposition concurring with the plastic substance of the protoplasm to nourish the plant.

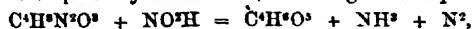
To separate the asparagine, aspartic acid, and succinic acid, the juice of the plant was boiled to separate albuminous matter; the filtered solution evaporated till it no longer deposited any crystalline substance on cooling; the solution saturated with sodium carbonate, then mixed with barium acetate and alcohol, which precipitated the succinic acid as barium salt; the alcohol evaporated; and the solution, somewhat diluted, was mixed with cupric acetate, which gave a precipitate of copper-asparagine. The liquid filtered from this precipitate was treated with hydrogen sulphide to precipitate the copper, then evaporated, and the residue was treated with sulphuric acid to convert the baryta into sulphate, and finally with ether, which on evaporation left a residue of aspartic acid (Mercadante, *Gazz. chim. ital.* 1875, 187).

Sachsse & Karmann have determined by Sachsse's method (2nd Suppl. 110) the percentage of asparagine in germinating peas during growth of various duration, both in the light and in the dark. The results are as follows:—

Duration of growth.	In light.	"	In darkness.
Six days	—		0.46
Ten "	0.69		0.55
Fifteen days	1.31		0.92
Twenty-four days	2.50		2.68
	6.04		7.04

Hence it appears that the absolute quantity of asparagine formed is the same in light and in darkness; but the weight of dry substance formed is greater in the light, and consequently there is a higher percentage of asparagine in the etiolated glands.

Asparagine is decomposed by nitrous acid, according to the equation:



the ammonia combining with the malic acid thus produced. The watery extract of peas, boiled and filtered to separate albumin and then treated with nitrous acid, yielded a quantity of nitrogen which showed that about one-third of the soluble nitrogen was in a form which gives the characteristic reactions of amides and amido-acids. As asparagine does not occur in ungerminated peas, the soluble body is, perhaps,

aspartic or glutamic acid, or more probably the substance analogous to asparagine found by Ritthausen in vetches.

The substance just mentioned was first obtained by Ritthausen (*J. pr. Chem.* [2], ii. 336) from the seeds of vetches grown in Greece; and he has since obtained 25 grams of it from 45 kilograms of seeds of black vetches grown near the Rhine. It forms feathery crystals having the composition $C^8H^{10}N^2O^8$, and is converted by nitric acid (sp. gr. 1.2) into a bulky gelatinous mass, very slightly soluble in water. On heating it, a small quantity of colourless gas is evolved, and a yellow solution is formed which, on evaporation over a water-bath, leaves an amorphous residue, violet-coloured at the edges. With fuming nitric acid, it evolves a large quantity of colourless and scentless gases, but the residue does not appear to contain malic acid (*J. pr. Chem.* [2], vii. 374).

Action of Urea on Asparagine.—When a mixture of equal parts of urea and asparagine is heated to 130° – 140° for half an hour, a transparent fused mass is obtained which dissolves in a small quantity of hot water, the solution, when left at rest for twenty-four hours, depositing a crystalline powder purifiable by recrystallisation. On heating the mother-liquors from which these crystals have separated to 100° for two or three hours, ammonia is given off, and the solution deposits another substance in transparent crystals (Guarzeschi, *Gazz. chim. ital.* v. 245).

On the influence of Asparagine contained in the Sugar-liquor from Beets and Canees on the Saccharimetric Determination, see STUART.

ASPARTIC ACID, $C^8H^{10}N^2O^8$. This acid is formed, together with uncrystallisable products, probably also consisting of amido-acids, by oxidising conglutin with potassium permanganate (R. Pott, *J. pr. Chem.* [2], vi. 91); also together with leucine, tyrosine, and a syrupy acid, by digesting blood-fibrin for some hours at 40° – 50° , with the pancreas of the ox (Radziejowski and Salkowski, *Deut. Chem. Ges. Ber.* vii. 1050).

ASPIRATOR. A new form of aspirator, founded on the principle of the diverging jet, is described by H. Lasne (*Bull. Soc. Chim.* [2], xix. 291; *Chem. Soc. Jour.* [2], xi. 837).

ATACAMITE. *Crystalline form.*—Crystals of this mineral from South Australia have been examined by v. Zepharovich (*Jahrbuch f. Min.* 1874, 83). Of the twenty-three forms previously observed in atacamite, these crystals exhibit eighteen. They are always prismatically elongated in the direction of the vertical axis and implanted by one end of it. At the free ends $P\infty$ is always present, and generally predominant; OP occurs frequently, P more rarely; ∞P is usually marked with long vertical striations, or curved. Mean sp. gr. = 3.76.

Zepharovich also gives a few observations on atacamite crystals from other localities, viz. (1) From Cornwall: so-called botallackite. The crystals have a twofold habit, being sometimes tabular and mostly terminated above by $P\infty$, laterally by ∞P , ∞P_2 and ∞P_3 ; or they are needles of the ordinary combination. (2) From Algodon Bay, Bolivia. Very thin, loose, somewhat curved lamellae terminated laterally by cleavage faces in the direction of $P\infty$.

From a new calculation of the dihedral angles of atacamite, v. Zepharovich deduces the axial ratio—

Macrodiaagonal.	Brachydiaagonal.	Principal axis.
1.6214	1	1.14086.

Composition.—Rammelsberg (*Mineralchemie*, 191) gives three varieties of atacamite, consisting of $CuCl^2.3CuO$, with 3, 4½ and 6 mols. H^2O respectively. A well-crystallised and apparently unaltered specimen from Australia, of a rich green colour and sp. gr. 4.314, analysed by J. A. Cabell (*Chem. News*, xxviii. 271) gave the following numbers:—

CuO .	Cu .	Cl .	H^2O .
55.64	14.67	16.44	12.02 = 97.77

which agree accurately with the formula $CuCl^2.3CuO.3H^2O$, or $CuCl^2.3CuH^2O^2$, or $Cu_2\{Cl(HO)^2\}$; also with the composition of a specimen of atacamite from Chile, analysed some years ago by J. W. Mallet, viz.—

CuO .	Cu .	Cl .	H^2O .	SiO^2 .
55.94	14.54	16.33	12.98	0.08 = 99.85.

The composition of normal atacamite appears, therefore, to be represented by the formula just given.

ATMOSPHERE. *Sources of Atmospheric Ammonia.*—From the known fact that the quantity of combined nitrogen supplied to the soil by rain and snow is less

than that which is removed by harvests and by drainage, Schloesing (*Compt. rend. lxxx. 175*) infers that some natural source of atmospheric ammonia must exist, independent of atmospheric electricity; and this he thinks may be found in the ocean, where the submarine organisms, growing at the expense of the enormous quantity of nitrates carried into the sea by rivers, yield up, when decaying in the absence of air, the whole of their nitrogen in the form of ammonia, which is directly absorbed from the air by plants and by the soil, without the interference of moisture. He calculates that from this source, a quantity of ammonia may be supplied to the soil, sufficient to repair the losses above mentioned. It must not be forgotten, however, that wherever nitrogen is removed from the soil by harvests or by drainage, it is found necessary to supply ammonia in the form of manure.

Quantities of Ammonia in the Air at different Heights.—P. Truchot (*Compt. rend. lxxvii. 1159*) has determined the quantities of ammonia in the air of Auvergne at three different heights, viz. at Clermont-Ferrand, 395 meters above the sea-level; on the Puy-de-Dôme at 1446 meters, and on the summit of the Pic de Sancy at 1884 meters. Two to 5 cubic meters of air were used for each determination.

At Clermont-Ferrand the results varied from 0.93 to 2.79 milligrams per cubic meter, the highest results being obtained on misty days, and the lowest on clear days.

The single determinations made on the Puy-de-Dôme on a bright day gave 3.18 m.g., and the results obtained at the higher elevation were 5.65 mg. on a day when the summit was covered with mist, and 5.27 mg. on a subsequent fine day. The general results appear therefore to be that the quantity increases with the elevation, and is greater in cloudy than in clear air.

On the Exchange of Ammonia between Air, Water, and Soil, see Schloesing (*Compt. rend. lxxxi. 81, 1252; lxxxii. 747, 846, 969; Chem. Soc. Jour. 1876, i. 95, 518; ii. 44, 172*).

Amount of Carbon Dioxide in the Air.—The determinations made by E. Schulze at Rostock (*2nd Suppl. 113*) gave results lower than the average of those of other observers, perhaps on account of the vicinity of Rostock to the sea. Similar results have, however, been obtained by Henneberg (*Landw. Versuchs-St. xvi. 70*) at Weend, near Göttingen. Seventeen determinations on a large scale gave a mean of 3.2 vol. CO₂ per 10,000 of air at 0° and under a pressure of 760 mm.

An average of 347 determinations made during a year at Duhme gave 3.34 vols. CO₂ in 10,000 volumes of air (Fittbogg a. Hasselbarth, *Chem. Centr. 1874, 694*).

Observations made by P. Truchot (*Compt. rend. lxxvii. 675*) in Auvergne gave for the most part higher results. The amount of carbon dioxide was determined by passing 10 litres of air through a solution of barium hydrate of known strength contained in four Woulfe's bottles, and by subsequent titration. The observations were made at Clermont-Ferrand during the months of July and August, both on an elevated terrace and in the country:—

		Carbon dioxide per litre. mgr.	Vol. in 10,000 air.		
On the terrace . . .	{ During the day . . .	0.701	3.58		
	{ During the night . . .	0.801	4.03		
In the country {	Remote from vegetation {	Day . . .	0.624		
		Night . . .	0.753		
	Near vegetation {	Day {	In the sun . . .	0.703	3.1
			In the shade . . .	0.825	4.15
		Night . . .		1.290	6.40

These figures show that the amount of carbon dioxide is larger during the night than in the daytime, and that the amount does not vary materially in the neighbourhood of a town. The sun influences the quantity of carbon dioxide near vegetation.

From observations made at different elevations it was found that the quantity of carbon dioxide diminishes considerably as the altitude increases.

Date	Place of Observation	Height	Temperature	Pressure	CO ₂ per litre at 0° and 760	Vol. in 100,000 air at 0° and 760
26th, 28th, 30th Aug., 1873	Clermont-Ferrand	395	52	725	0.623	3.13
27th Aug.	Top of Puy-de-Dôme	1446	21	638	0.405	2.03
29th Aug.	Peak of Sancy	1884	6	578	0.342	1.72

These results may be explained when it is considered that the carbon dioxide is evolved from the surface of the earth, and that its sp. gr. is greater than that of air.

Carbon Dioxide in the Air of the Soil.—The amount of this gas in the air of the soil of Munich, at different depths and at different times, has been determined by M. v. Pottenkofer (*N. Rep. Pharm.* xxi. 677). The soil from which the air was taken was a calcareous drift soil, containing sand and apparently free from organic matter. The air was extracted from it by means of five lead tubes, 1 centimeter in diameter, inserted to the depth of respectively 4, 3, 2½, 1½, and ¾ meters, the other end of each tube being connected with an aspirator. For each estimation of carbon dioxide, 14 to 18 litres of air was aspirated in about three hours. The experiments, which extended from September, 1870, to October, 1871, showed that the proportion of carbon dioxide in the air of the soil decreased with tolerable regularity from the lowest layer of the soil upwards, and that only the air in the upper layer was at all quickly influenced by the different rates of diffusion and ventilation, brought on by changes in temperature and increase of wind. During the greater part of the time, air was taken simultaneously from the depths of 4 and 1½ meters, ten or twelve experiments being made each month. The means of the quantity of carbon dioxide contained in 1000 parts of the air, by volume, in these comparable experiments, are given in the following table:—

1871.	CO ² in air from depth of 4 meters	CO ² in air from depth of 1½ meters	1871.	CO ² in air from depth of 4 meters	CO ² in air from depth of 1½ meters
January .	3·461	2·503	June . .	6·365	7·702
February .	4·176	2·428	July . .	8·072	8·805
March . .	4·106	2·786	August .	16·138	10·387
April . .	4·497	2·432	September .	14·016	9·037
May . .	5·777	5·402	October .	6·462	4·186

Only in the months of June and July did the air from the upper layer of the soil contain more carbon dioxide than that from the under layer. The maximum and minimum quantities in each layer occurred at about the same time.

The largest proportion of carbon dioxide corresponds with the greatest warmth in the upper layer of the soil.

Hydrostatic water was found at a depth of nearly 6 meters from the surface of the soil, and contained an almost constant quantity of 0·122 grams of free carbon dioxide per litre. In an experiment, made to find how much carbonic acid this bottom water could yield up to air lying immediately over it, 1034 litres of the water were allowed to drop through 9 litres of air contained in a flask, in the course of twenty-two hours; at the end of the experiment the air was found to contain 4·41 parts per 1000 of carbon dioxide; the air obtained from the soil at a depth of 4 meters, on the same day, containing 6·52 parts of carbon dioxide per 1000. In a similar experiment, but with 4300 litres of water passing through 7 litres of air, the air from the flask contained 4·54 parts, whilst air from the soil contained 7·03 parts of carbon dioxide per litre. These experiments, and other considerations, tend to show that the carbon dioxide in the air of the soil could not be derived from the bottom water, but that both the air and the water of the soil must obtain their carbon dioxide directly from the soil; they also suggest that the chief source of the carbon dioxide in this soil may be found in some of the lowest forms of animal life.

Hydrogen Peroxide in the Air.—E. Schöne (*Deut. Chem. Ges. Ber.* vii. 1693) has published a series of observations made in the latter half of the year 1874, on the presence and amount of this compound in the water precipitated from the atmosphere in every form (rain, hail, snow, dew, hoar-frost, &c.), and in artificial dew and frost obtained by exposing a vessel containing ice or a freezing mixture. The observations were carried on at the Agricultural Academy of Petrowskoje Rasumowskoje, near Moscow, and 180 meters above the sea-level.

The reagents employed were—

1. Potassium iodide, starch, and ferrous sulphate, which is capable of detecting 0·04 mg. per litre with difficulty; 0·05 mg. with certainty.
2. Guaiacum and malt extract, the limit of delicacy being 0·05 mg.
3. Ferric chloride and potassium ferricyanide, which will detect 0·02 mg. per litre, but is not so characteristic as 1 and 2, since ammonium nitrate produces the same reaction as peroxide of hydrogen. It is, however, decisive as to the absence of ozone.

4. Alkaline solution of lead oxide, lead acetate, potassium iodide, starch and acetic acid (Struve). This reagent does not distinguish the peroxide from ozone. The quantitative method was a colorimetric one, depending on the slow separation of iodine from potassium iodide in neutral solution.

Rain and Hail.—The quantity of peroxide varied generally between 0.04 mg. and 1 mg. per litre. In two cases, however, more than 1 mg. was observed. As a rule the smaller the drops of rain the less was the quantity of peroxide contained in them. After long dry weather the first rain that falls contains less peroxide than that subsequently falling, probably on account of the organic matters in the air, but during continuous rain the quantity generally diminishes considerably. In showers falling on the same day, at only short intervals, the proportion was often very different. The direction of the wind has an undoubted influence. The highest average was obtained with south and south-west winds. The amount also varies very considerably with the time of year. During the time occupied in the observations the quantity increased till the time of the autumnal equinox, and then diminished. The proportion in storm-rain appears to be on an average rather higher than in ordinary rain, but in individual cases the latter frequently exceeded the maximum in the former. The entire amount which fell on 1 square meter in four months was 62.9 mg. (in 221 litres of water).

Of twenty-nine samples of *snow* collected in November, twelve yielded indications of peroxide, with reagent 3 only. Of the remainder, none contained more than 0.05 mg. per litre (after melting). A dilute solution of the peroxide may be repeatedly frozen and thawed without loss.

Of all the samples of natural dew and hoar-frost, none contained sufficient peroxide to be detected by reagents 1 and 2.

The artificial dew and frost prepared during the night also yielded no indications, or at least only traces during the early part of the night; but it was present in that condensed after sunrise, and the quantity increased with the altitude of the sun to a daily maximum, which in July appeared to lie between 12 and 4 p.m., but became later as the days shortened, the quantity at the same time diminishing. Thus in July it was 0.4 mg.; in August, 0.35; in September, 0.15; and in October, 0.09 mg. per litre. Besides sunlight, which appears to be essential to its presence, the following meteorological conditions seem to favour a large proportion:—

1. A high temperature.
2. Absence of clouds.
3. High absolute and low relative moisture of the air.

After a fall of rain the amount in the artificial dew (or frost, between which there was no great difference) was $\frac{1}{3}$ (or less) of the quantity obtained in fine weather. This seems to indicate that the peroxide actually exists in the atmosphere in the form of vapour, and is washed out by the falling rain, and that it was not formed either at the moment of condensation or subsequently. This was corroborated by confining a condensation apparatus under a bell glass together with a vessel of water. The dew condensed under these circumstances contained no peroxide.

From the preceding data it is calculated that (assuming the whole of the peroxide to be precipitated together with the condensed water) the highest proportion obtained (0.4 mg. per litre) corresponds with $\frac{407}{10^{12}}$ gm. H^2O^2 , or $\frac{268}{10^9}$ c.c. of its vapour per litre of air.

Atmospheric Dust. G. Tissandier (*Compt. rend.* lxxviii. 821) has determined the amount of suspended matter in the air, by slowly drawing air by means of an aspirator through distilled water contained in Liebig's bulbs, and afterwards evaporating the water to dryness. In this way 6 mgrms. of dust was obtained from one cubic meter of the air of Paris, taken at a height of three meters from the ground, in three days after an abundant rain on the previous night. After continued dry weather in the summer, as much as 23 mgrms. were obtained from a cubic meter, but the ordinary amount was from 6 to 8 mgrms. From 1.5 to 3.5 mgrms. of dust was deposited, in different experiments, on a sheet of paper a square meter in area, exposed on a calm night, at a height of from 10 to 15 meters. The dust contained from 25 to 34 per cent. of organic matter, burning brilliantly; its composition may be fairly represented by the following analysis of dust taken from one of the towers of Notre Dame, into which no one had entered for several years:—

Organic matter	rich in carbon	32.265
Mineral matter	Soluble in water. Chlorides and sulphates of alkalis and alkaline earths and nitrate of ammonia	9.220
	Soluble in HCl	6.120
	CaCO ₃	15.940
	MgCO ₃ and traces of phosphates, alumina, &c.	2.121
	Insoluble in hydrochloric acid	34.334
		100.000

Iron, probably of extra-terrestrial origin, was present in all the samples examined.

ATOMIC VOLUME. See SPECIFIC VOLUME.

ATOMS. On the Absolute Weight of Atoms, see Annaheim (*Deut. Chem. Ges. Ber.* ix. 1151; *Chem. Soc. Jour.* 1877, i. 31).

On the Atomic Constitution of Bodies: Berthelot (*Compt. rend.* lxxxii. 1226); De Saint-Venant (*ibid.* 1223); *Chem. Soc. Jour.* 1876, ii. 471, 472.

On the Transposition of Atoms: Meyer & Forster (*Deut. Chem. Ges. Ber.* ix. 529). See also PROPYL NITRITES in this volume.

ATROPINE. *Preparation from Belladonna leaves.*—The leaves are exhausted with boiling water containing 10 grams tartaric acid per kilo. of the leaves; the filtered liquid is evaporated to dryness; and the residue repeatedly treated with strong alcohol at 50°. The alcoholic liquid is then distilled, and the residue shaken with ether, whereby gum and chlorophyll are removed, while atropine tartrate remains insoluble. Caustic potash solution is then added to the residue, which is again shaken with ether; the ethereal solution is evaporated; the residue dissolved in water acidulated with sulphuric acid; sodium bicarbonate is added; and the liquid again shaken with ether. On evaporating off the ether, pure atropine crystallises out (Lefort, *Chem. Centr.* 1873, 797).

Detection.—According to H. Brunner (*Deut. Chem. Ges. Ber.* vi. 96), the most characteristic tests of atropine are the dilatation of the pupil which it produces, and the aromatic smell which is emitted on adding the alkaloid and a little water to a hot mixture of sulphuric acid and potassium dichromate or ammonium molybdate. The latter reaction, although very characteristic, requires great skill; but it takes place without fail on placing the atropine on a few crystals of chromic trioxide contained in a porcelain basin, and applying a gentle heat until the trioxide assumes a green colour. (See further, *Chem. Soc. J.* 1876, i. 778.)

When an alkaline solution of atropine is shaken up with chloroform, the atropine dissolves in the chloroform even at ordinary temperatures (Newark, *Chem. Centr.* 1872, 536).

AUGITE. *Yellow Augite of Vesuvius.*—G. vom Rath (*Jahrb. f. Min.* 1876, 200) has examined a splendid bomb, 5 centimeters in diameter, from this locality, the outer crust of which consisted of saffordine, black augite, a little hornblende, and melanite. Below this crust, which was thin, there was a second zone, composed chiefly of green diopside and biotite; the interior of the bomb, however, was an aggregate of reddish augite, mica, and humite. The augite exhibited the combination $\infty P \cdot OP \cdot 2X\infty \cdot 2P \cdot P\infty \cdot \infty P\infty \cdot \infty P3$. Sp. gr. = 3.233. Its chemical composition was:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	Loss on ignition.
53.2	5.5	2.3	23.4	19.3	0.2 = 9.99

which agrees closely with the white or colourless varieties found at Achmatowak, Orrijärvi, Gulajö, &c. A remarkable fact connected with this augite from the Vesuvian bomb is that the outer augite contains only black augite; the druses of the second zone contain green augite, and those of the interior yellow augite.

A pseudomorphous conversion of augite into talc crystals has been observed in two distinct stages of conversion near Nordre Olafshy, in Snarum.

Some of these crystals, most of which are about 3 centimeters long and 1 centimeter broad, still cleave in one direction, possess a greenish-black colour, are transparent along their edges, and are not very hard. Other crystals have lost their capability of cleaving, are grey, and have the same hardness as talc. In some crystals there is found a nucleus which is still in the first stage of transformation. The chemical change involved in this latter pseudomorphosis consists in the replacement

of ferrous oxide and calcium oxide by water and magnesia (A. Helland, *Pogg. Ann.* cxlv. 480).

On the Molecular Volume of Augite, see VOLUME.

On Augite and Hornblende in Greenstone, see GREENSTONE (2nd Suppl. 581).

On Augitic Trachytes, see TRACHYTE.

AURANTIIN. The glucoside, found by De Vrij in the flowers of *Citrus decumana*, and regarded by him as hesperidin, is in reality quite a different body which may be called *aurantiin*. It crystallises in small, yellow, monoclinic prisms, dissolving freely in hot water and in 300 parts of cold water, and melting at 171° . The crystals consist of $C^{20}H^{20}O^{12} + 4H^2O$, and lose their water at 100° ; they have an intensely bitter taste, and give with ferric chloride a deep, brownish-red colour. Aurantiin fused with potash yields a product which gives with ferric chloride a green colour, not, however, due to protocatechuic acid (E. Hofmann, *Deut. Chem. Ges. Ber.* ix. 690).

AURIN, or ROSOLIC ACID, $C^{20}H^{14}O^8$ (Dale a. Schorlemmer, *Chem. Soc. J.* 1877, ii. 121). This red colouring matter, obtained by heating phenol with oxalic acid and sulphuric acid, has already been described (1st Suppl. 299; 2nd Suppl. 117). The experiments of Dale a. Schorlemmer last quoted left it undecided whether the true formula was $C^{20}H^{14}O^8$ or $C^{21}H^{14}O^8$. Recent experiments have shown, however, that a perfectly pure product may be obtained by heating a mixture of sulphuric acid and pure phenol on a water-bath, and adding the oxalic acid only gradually, always waiting till the evolution of gas has ceased before adding another portion, and not using sufficient to attack the whole of the phenol. Aurin thus prepared has exactly the composition $C^{20}H^{14}O^8$. In its formation, the oxalic acid is resolved into CO, CO^2 and H^2O , and the CO reacts with the phenol, according to the equation:



The same compound is obtained by the action of nitrous acid on rosaniline (1st Suppl. 999):



and it is reconverted into that base by heating with ammonia in aqueous or alcoholic solution:



From this it would appear that the true formula of rosaniline is $C^{20}H^{17}O^8$, whereas, according to Hofmann's analyses, it is $C^{20}H^{19}N^3$. Further experiments are required to reconcile this difference; but Dale a. Schorlemmer remark that, in the analysis of organic colouring matters, the percentage of hydrogen often comes out too high, a remarkable instance of which was exhibited in Schunck's analysis of alizarin from madder, which made the formula of that compound $C^{14}H^{19}O^4$, instead of $C^{14}H^{16}O^4$.

When aurin is heated with alcoholic ammonia for several days to 160° , the rosaniline which is first formed is converted into *leucaniline*, the alcohol in presence of alkali acting as a reducing agent. From this it might be inferred that a similar action takes place in the formation of rosaniline from aurin, thus—



But this is not the case, inasmuch as rosaniline is quickly formed by heating aurin with aqueous ammonia to 120° for 20 hours. If the temperature be raised to 180° – 200° , other colourless bodies are likewise formed, resembling those which Liebermann obtained by heating rosaniline with water.

Commercial aurin contains a large quantity of a pale red resinous body, as observed by Zulkowsky (*Deut. Chem. Ges. Ber.* x. 460), also a dark red colouring matter, which is not only much more soluble in alcohol than aurin, but also increases the solubility of the latter, which can be obtained pure only by a number of recrystallisations. None of these bodies are formed in preparing aurin from pure phenol according to the method above described.

AUTUNITE. Calcio-uranic Phosphate; see PHOSPHATES.

AVENTURIN ORTHOCLASE. See FELSPAR.

AZADIRACHTA. The bark of the Nim tree (*Azadirachta indica*) is commonly used in India as a tonic and febrifuge. Its taste is intensely bitter, that of the inner layer especially so. The leaves have also a very bitter taste, and are used externally as a poultice, being said to have a powerful effect in preventing glandular tumours from coming to maturity. The seeds yield a considerable amount of oil,

which also has a strong, bitter taste, and is used in medicine and for lamps. The roots are said to have vermifuge properties, but the main virtues of the tree reside in the bark.

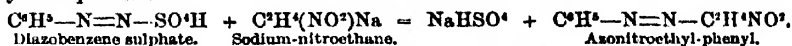
The bitter principle is a neutral resin, having scarcely any definite reactions. It may be obtained by exhausting the bark with alcohol of 60 per cent., precipitating the filtered tincture with water, and purifying the precipitate by solution successively in benzene, carbon sulphide, dry ether, and, finally, absolute alcohol. It is soluble in strong, boiling solutions of the fixed alkalis, from which acids reprecipitate it apparently unaltered. It does not form definite compounds with acids or with bases, but on treating it with nitric acid and precipitating with water, a nitro-derivative is obtained, having the composition $C^8H^4(NO^2)O^{11}$: hence the formula of the bitter principle is inferred to be $C^8H^4O^{11}$.

The leaves contain a small quantity of a bitter substance of a similar character, but much more soluble in water. This substance, also contained in the bark, is a hydrate of the resin, which it closely resembles in its properties (J. Broughton, *Pharm. J. Trans.* [3], iii. 992).

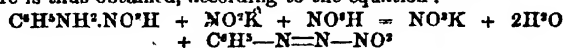
AZOBENZENE. See BENZENE.

AZOENZOIC ACID. See BENZOIC ACID.

AZONITROETHYL-PHENYL, $C^6H^4NO^2 = C^6H^4NO^2-N=N-C^6H^4$ (Meyer a. Ambühl, *Deut. Chem. Ges. Ber.* viii. 751, 1073). This compound is formed on mixing the aqueous solutions of diazobenzene sulphate and sodium-nitroethane, and separates as a yellow oil which soon crystallises. Its formation may be represented by the equation:



To prepare the compound it is not, however, necessary first to prepare a diazobenzene salt and the sodium-derivative of nitroethane. A much easier method is to dissolve aniline in exactly two equivalents of nitric acid, and add gradually with agitation, to the cooled and much diluted solution one equivalent of potassium nitrite dissolved in water. There is thus obtained, according to the equation:



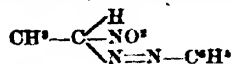
a solution of diazobenzene nitrate, mixed only with potassium nitrate, which, when gradually added to a recently prepared solution of nitroethane in an equivalent quantity of aqueous potash as long as a precipitate is formed, immediately throws down the azonitroethyl-phenyl.

This azo-compound is thus obtained, according to the concentration of the solutions used, either as a quickly solidifying oil, or at once in yellow flocks, which, by crystallisation from boiling alcohol, are converted into golden-yellow laminae, very much like chloranil. It dyes silk a pure and deep golden-yellow. When not quite pure it is unstable, the crystals, after a few weeks, suddenly becoming resinised, and giving off red vapours.

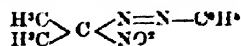
Azonitroethyl-phenyl is a well-characterised acid, forming salts containing 2 atoms of univalent metal. The *potassium salt*, $C^6H^4N^2O^2K^2 + 4H^2O$, obtained by triturating the substance with alcoholic potash and washing the resulting crystalline mass, first with alcohol, then with ether, forms orange-yellow laminae. The *sodium salt*, $C^6H^4N^2O^2Na^2 + 7H^2O$, is prepared in like manner and exhibits similar characters. The *zinc salt*, $C^6H^4N^2O^2Zn + 3H^2O$, is obtained as a chrome-yellow precipitate on mixing the aqueous solution of the potassium salt with zinc chloride. *Lead salts*, probably of variable composition, are obtained, sometimes as brownish-yellow, sometimes as brick-red precipitates. The brick-red salt is basic, and has the composition $C^6H^4N^2O^2Pb.PbO + 2H^2O$.

The *silver salt* is a red-brown precipitate which easily turns black and decomposes. All these salts, when decomposed by hydrochloric acid, give up the azonitroethyl-phenyl in its original state.

The apparent bibasicity of this compound is remarkable, inasmuch as the formula



should contain only one atom of hydrogen replaceable by metals, namely, that which is contained in the group $CH(NO^2)N^2$; and in fact, the corresponding pseudopropyl compound:



188 AZONITROETHYL-PARATOLYL—AZONITROPHENIN.

in which the corresponding hydrogen atom is replaced by methyl, possesses no acid properties whatever (see below).

Regarding, therefore, azonitroethyl-phenyl as a monobasic acid, the salts above described must be looked upon as basic salts, thus:

Potassium salt	$C^6H^4N^2O^2.K.KOH + 3H^2O$
Sodium salt	$C^6H^4N^2O^2.Na.NaOH + 6H^2O$
Zinc salt	$C^6H^4N^2O^2.Zn.OH + 2H^2O$
Lead salt	$C^6H^4N^2O^2.Pb.OH + 1\frac{1}{2}H^2O$

Azonitroethyl-phenyl, boiled with fuming hydrochloric acid, gives off a third of its nitrogen as gas, and yields a colourless base, the hydrochloride of which is extremely soluble in water and alcohol, and has a tendency to resinise, so that its exact composition is not easily ascertained; its analysis, however, indicates the formula $C^6H^4N^2O^2.Cl$.

Azonitroethyl-phenyl is reduced by tin and hydrochloric acid, but the product of the reaction is mixed with that resulting from the action of the hydrochloric acid alone.

Bromine forms with azonitroethyl-phenyl a well-crystallised compound which decomposes very early, with formation of bromobenzene.

AZONITROETHYL-PARATOLYL, $C^6H^4NO^2-N=N-C^6H^4(CH^3)$, (Barbieri, *Deut. Chem. Ges. Ber.* ix. 386). This body is obtained by the action of diazoparatolyl nitrate on nitroethane. It forms fine orange-red prisms, having a peculiar steely lustre, and melting at 133° . In other respects, it closely resembles azonitroethylphenyl. It dissolves in alkalis, forming deep-red salts. An aqueous solution of the sodium salt gives coloured precipitates (yellow to red) with mercury, silver, lead, copper, and zinc salts.

Azonitroethylorthotolyl is obtained like the foregoing substance, which it resembles in properties. It crystallises in orange needles which melt at $87^\circ-88^\circ$.

AZONITROMETHYL-PHENYL, $CH^3(NO^2).N^2.C^6H^5$, is obtained like the ethyl-compound, but to avoid the formation of resinous bodies, the solutions must be very dilute. The compound separates as a cherry-red oil, which soon solidifies. It crystallises from alcohol in fine red needles having a brilliant silky lustre, and from carbon sulphide in prisms resembling chromic trioxide. At 163° it melts and decomposes, and when more strongly heated it deflagrates. In concentrated sulphuric acid it dissolves with intense purple colour; water reprecipitates the unaltered compound.

It is more stable than the ethyl-compound, being decomposed by hydrochloric acid only after prolonged boiling. The product is a compound which, by evaporation and recrystallisation, is obtained in long white spicular crystals having a silky lustre (Fries, *Deut. Chem. Ges. Ber.* viii. 1080).

AZONITROPSEUDOPROPYL-PHENYL, $C(CH^3)_2(NO^2).N^2.C^6H^5$, formed by adding an aqueous solution of diazobenzene nitrate to a recently prepared solution of pseudonitropropane in potash-ley, separates as a yellow oil which does not solidify. It is heavier than water, does not volatilise either alone or with vapour of water, and is quite insoluble in alkalis (Meyer a. Ambuhl, *Deut. Chem. Ges. Ber.* viii. 1076).

AZOPHENIN, $C^6H^3N^2O$ (Kimich, *Deut. Chem. Ges. Ber.* viii. 1026). This compound is formed, together with other products, by the action of nitrosophenol on aniline:



Nitrosophenol, mixed with excess of aniline acetate, sets in a few days, or if warmed on the water-bath, in half-an-hour, into a black crystalline mass, from which, after washing with water, dilute ammonia extracts oxyazobenzene, leaving a residue containing azophenin; and on exhausting this residue with alcohol, washing it with a little benzene, and then crystallising it repeatedly from toluene and xylene, azophenin is obtained in red scales, insoluble in alcohol, ether, and alkalis, melting at 224° , and decomposing at a higher temperature, with formation of several products not yet examined. By tin and hydrochloric acid it is reduced to a yellow crystallisable base.

Azophenin is also produced, together with a large quantity of viscid substances, by the action of nitrosodimethyl-aniline on aniline acetate.

A compound, $C^6H^3N^2O$, homologous with azophenin, is formed by the action of nitrosophenol on paratoluidine. It forms red scales melting at $249^\circ-260^\circ$, and closely resembling the aniline compound. Its behaviour when heated is, however, quite different, for it does not yield a crystalline sublimate, and no definite compound can be extracted from the residue.

AZOPHENYLENE, $C^{12}H^8N^2 = C^6H^4=N-N=C^6H^4$ (Claus, *Deut. Chem. Ges. Ber.* viii. 37, 600). This compound is most conveniently obtained from the brown product of the dry distillation of calcium azobenzoate. On dissolving this substance in alcohol saturated with ammonia, and passing sulphuretted hydrogen into the solution, nearly pure hydrazophenylene is precipitated, which, by sublimation, yields perfectly pure azophenylene.

Azophenylene is not formed from azobenzene by passing the latter through red-hot tubes, however the conditions of the experiment may be varied. At a high temperature, the products of the decomposition are free from nitrogen, and consist of diphenyl, anthracene, and chrysene. Dinitrophenyl does not yield azophenylene, either when treated with alcoholic potash or heated with zinc-dust, neither is azophenylene obtained from benzidine by oxidation with permanganate or with chromic acid.

Pure azophenylene melts at 171° , boils at a temperature above 360° , and does not form a sulphonic acid, as previously stated by Claus.

Azophenylene dichloride, $C^{12}H^8N^2Cl^2$, is obtained in red crystals by passing dry chlorine into a solution of azophenylene in absolute alcohol. It is very unstable, being easily resolved into its constituents.

Azophenylene hydriodide, $C^{12}H^8N^2HI$, is prepared by heating the two compounds together for several days to 120° . It crystallises in dark-green needles, and is decomposed by water.

Azophenylene hydrobromide, $C^{12}H^8N^2HBr$, is obtained by evaporating a solution of azophenylene in concentrated hydrobromic acid. It forms brown crystals.

Azophenylene hydrochloride, $C^{12}H^8N^2HCl$, is easily formed by boiling azophenylene with hydrochloric acid. It crystallises in rhombic prisms or plates. It is decomposed by water, and on adding platonic chloride to its solution in hydrochloric acid, small golden-yellow needles of $(C^{12}H^8N^2HCl)_2PtCl^4$ are precipitated. It also combines with auric chloride, forming a yellow precipitate, $C^{12}H^8N^2HCl.AuCl^3$. On adding mercuric chloride to a hot solution of azophenylene in hydrochloric acid, the compound $(C^{12}H^8N^2HCl)_2HgCl^2$ separates on cooling in brownish crystals.

Nitrate of azophenylene has not been obtained; but by dissolving azophenylene in hot nitric acid, and adding mercuric nitrate, ruby-red crystals are obtained, having the composition $C^{12}H^8N^2.Hg(NO^3)^2$. By the action of hydrogen sulphide on the solution of this compound, a dark-green precipitate is formed, containing mercury in combination with hydrazophenylene. The corresponding silver compound, $C^{12}H^8N^2(AgNO^3)^2$, is a heavy yellow precipitate, crystallising from hot nitric acid in golden-yellow plates, which deflagrate when heated.

Mononitrazophenylene, $C^{12}H^7(NO^3)N^2$, is formed by dissolving azophenylene in a mixture of fuming sulphuric and nitric acids, and boiling the mixture for eight hours; the addition of water precipitates the pure nitro-compound in slender greenish-yellow needles, which melt at 209° to 210° , and sublime without decomposition at a higher temperature. It is reduced by sulphuretted hydrogen in ammoniacal solution, finally yielding a red product, probably amidazophenylene. The action of fuming nitric acid on azophenylene in alcoholic solution yields a mixture of substances, in which there appears to exist a *dinitrazophenylene*, $C^{12}H^6(NO^3)^2N^2$, melting at 131° .

Dichlorazophenylene, $C^{12}H^6Cl^2N^2$.—The action of phosphorus pentachloride on azophenylene gives rise to a number of products, one of which, melting at 144° , appears to have this composition.

AZOTOLUENE. See **TOLUENE**.

AZURITE. See **CARBONATES OF COPPER**.

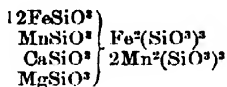
B •

BABINGTONITE. This mineral has been found among the slag in the manufacture of Bessemer steel, forming small greenish-black crystals, of sp. gr. 3.24 and hardness 6.

Its composition (compare 2nd Suppl. 122) was found to be—

SiO.	Fe ^o O.	Mn ^o O.	FeO.	MnO.	CaO.	MgO.
48.896	5.338	10.908	29.485	2.386	1.807	1.431 = 100.250

leading to the formula :—



For the estimation of ferrous in presence of ferric oxide, the mineral was decomposed by hydrofluoric acid in an atmosphere of carbon dioxide, and titrated with potassium permanganate. The manganous oxide, in presence of manganic oxide, was determined by dissolving the whole in ammonium chloride, and precipitating the manganic oxide by ammonia, which does not precipitate pure manganous oxide from such a solution (H. Klemm, *Chem. Centr.* 1874, 215).

BOO. *Bambusa arundinacea*.—The ash of bamboo-stems has been analysed by Hammerbacher (*Liebig's Annalen*, clxxvi. 87), with the following results :—

SiO ² .	CaO.	MgO.	K ² O.	Na ² O.	Cl.	SO ² .	Ferric Phosphate.
28.264	4.481	6.669	34.217	12.765	2.062	10.705	0.037 = 99.100.

The ash is rich in silica and alkalis, poor in alkaline earths. The proportion of alkalis is about the same as the ashes of ordinary woods.

BANCOUL NUTS. See ALEURITES (p. 54).

BAPHIA. An investigation of the educts from barwood (*Baphia nitida*) was made by the late Dr. Thomas Anderson (*Chem. Soc. J.* 1876, ii. 583). To obtain them, the wood, after being torn to a fine dust, is placed in a digesting apparatus, and exhausted thoroughly with anhydrous 'methylated' ether free from alcohol. The liquid which traverses the wood gradually diminishes in colour as the extraction proceeds, until, from having been strongly red, it becomes almost (though never quite) colourless. This liquid is heated in the water-bath, to drive off the greater part of the ether. The residue, left to itself for a short time in a cool place, may deposit a small quantity of baphic acid, in the form of platy crystals. These are separated from the mother-liquid, in which they are quite insoluble; the latter is evaporated so as to drive off the greater part of the ether, and then mixed with alcohol. After an interval varying from one to several days, a crystalline magma forms, consisting of baphiin, contaminated with a solid red colouring matter, and containing also some dark and viscous tinctorial substance which has not been examined.

The wood, thoroughly freed from ether by evaporation, is next exhausted with alcohol, and the alcoholic liquid is distilled nearly to dryness and left at rest, whereupon it solidifies after long standing, to a semicrystalline mass, containing (as in the case of the ethereal extract) a viscous colouring matter of a deep-red colour. The mass, on exposure to air, dries up, with fission, to a granular powder. Its crystalline constituent has not been examined.

The use of other solvents than those above mentioned is not satisfactory. Benzene and carbon disulphide, at about 100°, have the advantage of dissolving scarcely a trace of the colouring matters, but, on the other hand, the disadvantage of extracting only a very trifling quantity of the colourless ingredient, baphiin. Any baphic acid that may be present, is, however, removed by the hot benzene with tolerable facility.

Baphin, $\text{C}_9\text{H}_7\text{O}_4$, obtained, as above mentioned, from the ethereal extract of the wood, and purified by repeated crystallisation from strong spirit, is a colourless substance having an odour of orris root. • It crystallises from alcohol in plates of

considerable lustre, from ether, by rapid evaporation, in tufts of needles. It is but very sparingly soluble in benzene and in carbon disulphide; insoluble in water. When allowed to crystallise from its solution in alcohol on a finely divided surface in presence of air, it rapidly oxidises, producing colours which vary from yellowish-red to light purple. When heated it melts partly below 200° , partly at a higher temperature, indicating decomposition. Dried at 100° it yields by analysis (mean 66.40 per cent. carbon and 4.9 hydrogen) the formula $C^{24}H^{20}O^4$, requiring 66.05 C. and 4.59 H.

An alcoholic solution of baphiin, mixed with alcoholic lead acetate, forms a white precipitate of lead baphate, which turns brown in drying, probably from oxidation; and the alcoholic filtrate, mixed with water, yields a crystalline precipitate of baphinitin. With dilute aqueous potash at the boiling heat, baphiin reacts in the same manner as with alcoholic lead acetate; with strong potash-ley other products are formed (*infra*).

The resolution of baphiin into baphic acid and baphinitin is analogous to that of athamantin into valeric acid and oreoselone (iv. 216).

Baphic Acid, $C^{24}H^{20}O^5$ or $C^{24}H^{22}O^{10}$, prepared by boiling baphiin with aqueous potash, filtering and adding hydrochloric acid, is precipitated as a yellowish-white powder, and may be purified by placing it on the filter (without washing), drying in the air, extraction with anhydrous ether, evaporation of the ethereal solution, and repeated crystallisation. It then forms white nacreous scales very soluble in alcohol, still more in ether, insoluble in water. Its alcoholic solution instantly precipitates metallic silver from the nitrate.

Baphinitin, nC^4H^4O , is the chief product obtained by boiling baphiin with aqueous potash; it is also found in the mother-liquor remaining after the precipitation of lead baphate from a mixture of the alcoholic solutions of baphiin and lead acetate. It is white, smells like baphiin, but more strongly; is insoluble in water, but dissolves with moderate facility in alcohol and ether; and crystallises in needles. Treated with strong sulphuric acid, and afterwards with water and barium carbonate, it forms a solution from which sulphuric acid precipitates barium sulphate, the mother-liquor yielding on evaporation a deliquescent barium salt.

Baphinitone, $C^{24}H^{22}O^6$.—When baphiin is boiled with strong aqueous potash, air being excluded as much as possible during the operation, there is left undissolved a mixture of three substances:—(1) baphinitin, which dissolves in alcohol and ether with moderate ease; (2) baphinitone, which is very easily soluble in these liquids; and (3) a small quantity of an unexamined body, fusible at 184.1° (corr.), very sparingly soluble in alcohol, even when hot, and separating therefrom in granular crystals. Baphinitone is prepared by treating the portion of baphiin insoluble in aqueous potash with cold alcohol, which readily dissolves the baphinitone, and but little baphinitin. The solution is evaporated and the treatment repeated, till the crystals thus obtained, after drying over sulphuric acid, melt at or near 88° . Baphinitone crystallises from alcohol in hemispherical masses, composed of radiating crystals, beautifully white and lustrous, insoluble in water. It gave by analysis 71.67 per cent. C. and 6.36 H., the formula requiring 71.89 C. and 5.99 H.

Tribromobaphinitone, $C^{24}H^{22}Br^3O^6$, is obtained by treating an ethereal solution of baphinitone with an ethereal solution of bromine, and remains on evaporating off the ether, as a white substance, which may be purified by washing with alcohol or ether, in both of which it is almost insoluble. It separates from a hot ethereal solution in small granules, melting with sudden blackening, at 180.2° (corr.)

Baphiin, baphinitone, and the substance least soluble in alcohol which occurs with the latter, are all coloured orange-yellow by sulphuric acid; with nitric acid an orange-red is obtained, changing to green.

The molecular formulæ of these bodies are somewhat complex, and not easy to determine. Taking, however, that of baphinitone to be precisely determined, a C^{24} -formula may with great probability be assumed for all these bodies, as in the following series:—

Baphiin	$C^{24}H^{20}O^4$
Baphic acid	$C^{24}H^{22}O^{10}$ [(?)]
Baphinitin	$C^{24}H^{24}O^8$
Baphinitone	$C^{24}H^{22}O^6$

Colouring Matters.—Barwood contains at least three colouring matters. Ether dissolves out two of these: one (A) which is less soluble, and obstinately adheres to the baphiin, and another more soluble (B), which is easily got rid of. After the extraction with ether is complete, alcohol dissolves a third (C). All are insoluble in

benzene; all give purple lakes with lead acetate, and purple colorations with alkalis.

(A.) The solubility of this body in ether diminishes after exposure to air. It may be purified from baphiin by boiling with benzene, in which the latter dissolves. It is a bright red powder.

(B.) Crystalline; dissolves easily in boiling alcohol. A strong solution cuts off the blue, and nearly all the green of the spectrum—the blue first. The same solution, mixed with hydrochloric acid, becomes darker, transmits the blue faintly, and very much obscures the green; the yellow and red are transmitted. The solution, after the addition of the acid, becomes deep-pink on mixing with ammonia or potash; the green and blue are much obscured, while the red is left, and the yellow is cut off, and replaced by a black band.

(C.) The green is more absorbed by this colour in alcoholic solution than by (A). When the solution is moderately strong, a black band appears in the yellow. When hydrochloric acid is added, the green is more obscured, and the yellow is still decidedly effaced, notwithstanding the dilution; the blue is nearly removed; the red remains. When ammonia is added to the solution after the action of hydrochloric acid, the colour becomes deep-purple; the red ray is transmitted, the yellow is effaced, the green scarcely visible. Acts on the green and yellow more than A.

The results above detailed do not corroborate the statement sometimes made, that the 'colouring matter' of barwood is identical with santonin.

BARIUM. *Occurrence in Nile Mud and in Egyptian*Wheat.*—Knop has found 0.021 and 0.017 per cent. of barium carbonate in Nile mud from Minieh and Achmin respectively (*Landw. Versuchs.-St.* xvii. 66). The occurrence of barium in this deposit has been confirmed by H. Dworczak (*ibid.* 398), who has also found it in the ash of wheat grown thereon. The leaves were found to contain a larger proportion than the stem, in which respect the distribution of barium in this wheat is analogous to that of calcium in the generality of plants.

In Furnace dust.—The presence of barium has been demonstrated both by the spectroscopic and by chemical analysis in the dust of the Silesian zinc furnaces (Schwarz, *Dingl. pol. J.* ccxviii. 219).

Preparation.—Metallic barium may be prepared by decomposing the iodide with sodium, dissolving out the reduced metal with mercury, and distilling off the mercury. The reaction between the barium iodide and the sodium is attended with incandescence (Kern, *Chem. News*, xxxi. 243).

Separation from Strontium and Calcium.—According to Kümmerer (*Zeitschr. anal. Chem.* xii. 375) the best method for the qualitative separation of barium from strontium and calcium as barium chromate is to dissolve the carbonates, obtained by precipitation with ammonium carbonate, in acetic acid, and then add potassium chromate. The presence of ammonia salts is to be avoided, as they increase the solubility of barium chromate.

From analyses by Fr. Frerichs (*Deut. Chem. Ges. Ber.* vii. 800) it appears that this method may also be applied to the quantitative separation and estimation of barium, in presence of calcium, strontium, or magnesium.

Volatility at High Temperatures.—When anhydrous baryta is intensely heated in a wind-furnace in contact with aluminium in the form of ingot or in filings, a portion of it (1.97 and 1.76 per cent. in two experiments) is volatilised and is found, partly mixed with the metallic aluminium, as aluminate or oxide, partly in the remains of the anhydrous baryta, partly in the crucible and its cover. The reduction and volatilisation of the metals are further demonstrated by observing with the spectroscope the carbon monoxide flame of the furnace (heated with the hard carbon deposit from coal-gas retorts). Strontium and calcium may be volatilised in the same way (J.W. Mallott, *Chem. Soc. Jour.* 1876, ii. 354).

Barium Hydrate.—On the economical preparation of the hydrates of barium, potassium, and sodium from the corresponding sulphides, see Tessié du Mothay (*Dingl. pol. J.* cccv. 333; *Chem. Soc. Jour.* [2], xi. 414).

Reactions with Carbon Disulphide.—Baryta-water agitated with carbon disulphide yields a basic sulphocarbonate, $\text{BaCS}^2 \cdot 2\text{BaH}^2\text{O}^2 + 6\text{H}^2\text{O}$, soluble in alcohol and in carbon disulphide, slightly soluble in cold water, and decomposed by acids, with liberation of sulphocarbonic acid, CS^2H_2 , in oily drops (D. Walker, *Chem. News*, xxx. 28).

Peroxide.—According to E. Schöne (*Deut. Chem. Ges. Ber.* vi. 1132) hydrated barium peroxide, prepared according to the original method of Thénard, has the composition $\text{BaO}^2 \cdot 8\text{H}^2\text{O}$, and forms microscopic crystals, belonging to the quadratic system, usually exhibiting the combination, ∞ P.O.P, sometimes tabular from pre-

dominance of OP, and having the prismatic edges truncated by $\infty P \infty$. The hydrated dioxides of calcium and strontium are isomorphous with it.

Rammelsberg showed in 1869 (*Deut. Chem. Ges. Ber.* ii. 147) that the product obtained by ignition of barium nitrate contains more oxygen than the monoxide; and by further experiments (*ibid.* vii. 542) he finds that the grey porous mass contains, on the average, 86.4 per cent. barium, agreeing nearly with the formula Ba^2O^4 , or $2BaO.BaO^2$, which requires 86.5 per cent.

The oxygen in this and similar bodies cannot be estimated by the iodometric method, as on heating them, even with strong hydrochloric acid, only a small quantity of chlorine is evolved, not more than sufficient to impart a yellow colour to a solution of potassium iodide. The estimation may, however, be effected, as shown by Aschoff (*J. pr. Chem.* lxxxi. 401), by means of potassium permanganate, which, in contact with H^2O^2 , is resolved into MnO and free oxygen, in such a manner that the two compounds yield equal quantities of oxygen.

Barium dioxide, BaO^2 , contains by calculation 81.06 per cent. Ba and 18.94 O. A preparation containing 78.9 per cent. barium was found by the preceding method to approach more nearly in composition to Ba^2O^4 than to BaO^2 .

1 (Fr. Orge, Ger. Gerste). The various species of cultivated barley are distinguished as two-rowed, four-rowed, and six-rowed, according to the number of fertile spikelets. The first and last of these species are the most characteristic, the six and the four-rowed being nearly related. *Hordeum distichum* (two-rowed barley) includes the finest varieties of English barley. *H. hexastichum* (six-rowed barley) includes the 'bere' or 'big' of Scotland, which is also four-rowed, and several varieties largely grown in the north of Europe. The *H. vulgare* of Linnæus is a four-rowed barley. Varieties of each of these species occur, in which the chaff separates readily from the grain, as in wheat; these are known as naked barley, *H. calcarata*, *Himmelsgerste*, &c. Naked barley possesses as high a weight per bushel as wheat.

The composition of barley, like that of oats, exhibits a wide range of variation, which is largely due to the varying thickness of the adhering chaff. The finer qualities, having the plumpest grain and thinnest chaff, are those used for preparing pearl-barley, and for malting; the inferior qualities, ground as meal, serve as food for pigs and cattle.

The following table shows the general percentage composition of barley grain and straw, with the extent of variation observed, deduced from a compilation of all accessible analyses. The single analysis of bere is by Anderson; that of naked barley by Lejeune, from a sample grown in Algeria; the analysis of barley chaff is quoted from Wolff.

	Number of analyses	Water	Albuminoids	Fat	Carbo-hydrates	Fibre	Ash
Barley, mean composition .	56	14.05	10.58	2.05	63.66	7.09	2.57
„ highest percentages .	—	18.96	15.72	2.60	71.49	13.49	4.70
„ lowest percentages .	—	11.66	6.91	1.41	54.40	2.31	2.06
Bere .	1	14.22	10.25	62.85	10.08	2.60	
Naked barley	1	10.77	8.76	1.81	74.70	2.03	1.93
Barley chaff		14.30	3.00	1.50	38.20	30.00	13.0
Barley straw, mean comp. .	13	16.00	3.06	1.57	32.49	41.84	5.04
„ highest percentages .	—	17.50	5.37	1.99	39.59	66.54	6.16
„ lowest percentages .	—	9.65	1.05	1.17	8.21	36.52	4.93

The greater part of the nitrogen in ripe barley straw is contained, according to C. Schneider, in the leaf and leaf-sheath; the empty ear is also comparatively rich in nitrogen. In the true stem he found but 0.14 per cent. of nitrogen in the dry substance.

Barley grain contains on an average less nitrogen than either wheat or oats; the proportion is least in fine malting barley, amounting to only 8 or 9 per cent. of albuminoids, but is greater in the inferior samples used for grinding into meal. The composition of barley-meal is the same as that of the barley from which it is made, no separation of parts being effected.

Some light is thrown on the arrangement of the constituents in barley grain by analyses of the various products obtained in making pearl-barley. In this manufacture the outer layers of the grain are successively removed. The first product contains the bulk of the chaff, and is known as 'coarse dust.' The second product consists of a

little chaff, and the layer immediately beneath it; it is known as 'fine dust.' The grain thus denuded of chaff is termed Scotch or pot-barley. By a third treatment in the mill, pearl-barley of various qualities is produced, the quality being higher in proportion as the grinding is carried further. The matter removed at this period of the grinding is known as 'pearl dust.' One hundred parts of good barley yield on an average $12\frac{1}{2}$ of coarse dust, $14\frac{1}{2}$ of fine dust, $25\frac{1}{2}$ of pearl dust, and $37\frac{1}{2}$ of pearl-barley, the remainder being lost in grinding. The following analyses of the various products were made by Professor Church upon samples from the mills of Messrs. Hays, Leith:—

	Coarse dust	Fine dust	Pearl dust	Pearl Barley
Water	14.18	13.05	13.33	14.67
Albuminoids	6.97	17.58	12.11	7.32
Fat	1.70	6.00	3.44	1.15
Carbo-hydrates . . .	46.88	50.54	67.18	75.21
Fibre	24.57	8.53	1.83	.60
Ash	5.70	4.30	2.15	1.05

It is evident that the layer immediately below the chaff is extremely rich both in albuminoids and fat, and that the proportion of these constituents diminishes rapidly towards the centre of the grain, which contains a much larger proportion of starch. The ash follows the same order, and diminishes greatly from the exterior to the centre. Pearl-barley evidently contains only a very small proportion of albuminoids; in a second sample Church found only 6.22 per cent.*

The embryo of barley grain is singularly rich in albuminoids and fat. Haberland found in the dry germ of naked barley 22.42 per cent. of fat, and Lenz, in similar forms, 5.0 per cent. of nitrogen.

The nature of the albuminoids in barley grain has been investigated by Kreusler; he finds them to be a mixture of gluten-casein, gluten-fibrin, mucodin, and albumin, the last being comparatively small in quantity. Gliadin is apparently not present (*Die Eiweisskörper der Getreidearten*, 104).

[For the percentage composition of the fat of barley, see 2nd Suppl. 507.]

The carbo-hydrates of barley grain are at present under investigation. Kühnemann (*Deut. Chem. Ges. Ber.* viii. 389; ix. 1385) states that they include a laevorotatory body, sparingly soluble in hot water, and separating as a turbidity on cooling; it resembles dextrin when dry. To this body he has given the name sinistrin. He also finds in barley a crystallisable, dextrorotatory sugar, not capable of reducing copper, agreeing, therefore, with sucrose in its properties. As chemists have generally employed a copper solution to determine the sugar in grain, the quantitative results hitherto published are of little value. Kühnemann finds no dextrin in barley grain. The hordein of earlier chemists is undoubtedly a mixture.

The following table shows the percentage composition of the ash of barley—sand, and charcoal, and carbonic acid, if present, being deducted. The mean composition of the ash of barley grain is calculated from the 50 analyses quoted by E. Wolff (*Aschen Analysen*, 17), with the addition of 1 by Lenz, and 10 unpublished analyses by R. Richter. The analyses of the ash of coarse and fine dust are by Anderson. Two of those of naked barley are by Bifra and 1 by Schulze. The analyses of straw ash are the 21 quoted by Wolff, with 8 unpublished analyses by R. Richter. The analysis of the awn is by Way. The analyses of the entire plant are 1 by Scheven, and 5 by Wolff.

* The total albuminoids present in vegetable products is commonly ascertained by multiplying the nitrogen found by 6.25; Ritthausen, however, points out (*Die Eiweisskörper der Getreidearten*, 286) that recent investigations into the composition of vegetable albuminoids would rather lead to the factor 8.00 being employed; the numbers given above should, therefore, possibly be reduced to the extent indicated. Another point to be borne in mind is that a part of the nitrogen exists in other forms than albuminoids, and that the latter are on this account always reckoned too high. Church, by his carbolic method, found that 7.9 per cent. of the total nitrogen in the pearl barley last mentioned did not exist as albuminoids.

	Num- ber of anal- yses	Pure ash in dry	K ² O	Na ² O	CaO	MgO	Fe ² O ³	P ² O ⁵	SO ³	SiO ²	Cl
Barley grain, mean .	61	2.57	21.35	2.25	2.74	8.66	.91	35.19	1.72	26.10	.88
highest percentages		3.09	32.20	6.00	4.35	12.73	2.93	42.56	3.50	36.73	5.24
lowest percentages .		1.90	11.39	none	1.21	5.00	none	26.01	none	17.27	none
Coarse dust .	1	5.63	16.81	1.40	3.71	6.27	1.69	18.45	1.92	48.73	1.25
Fine dust .	1	2.32	28.64	1.99	2.39	12.05	1.42	50.15	.06	2.81	none
Naked barley .	3	2.13	28.47	1.84	3.13	12.00	1.94	47.09	2.89	3.64	none
Barley straw, mean .	29	4.85	21.56	4.24	8.50	2.48	.82	4.40	4.00	51.49	3.21
highest percentages		7.42	44.46	13.42	13.10	5.70	2.91	7.20	8.01	68.50	16.31
lowest percentages .		2.97	10.76	1.03	5.34	1.31	none	1.88	.80	32.11	none
Awn .	1	13.95	7.86	.96	10.57	1.29	1.49	2.03	3.05	72.20	.68
Entire ripe plant .	6	5.78	18.71	1.23	4.29	2.80	.51	10.74	2.55	57.25	2.48

The ash of barley grain differs from that of wheat chiefly by reason of the large amount of silica contained in the adhering chaff; the ashes of naked barley and of wheat are quite similar in composition. In respect of its proportion of silica, barley holds an intermediate position between wheat and oats. The ash analyses of coarse and fine dust (the latter possibly pearl dust) illustrate the difference in composition between the exterior and inner layers of the grain; the former is rich in silica, and contains a larger proportion of lime than the latter. Silica and lime are commonly associated in the vegetable world as the incrusting matters of external surfaces. The awns attached to barley grain are seen to contain a large proportion of ash, nearly three quarters of which is silica, lime being the next preponderating constituent.

The ash of barley straw contains more potash, rather more lime, and much less silica than the ash of wheat straw. The ashes of barley and oat straw are quite similar in composition.

It must be recollected that ~~is~~ ashes containing much silica, as those of barley grain and straw, the chlorine is liable to be under-estimated, being expelled by the silica when the temperature of incineration has been high. Scheven found considerably more chlorine in the sap than he obtained by incinerating the entire barley plant. The sulphuric acid in the ash also bears no constant relation to that in the original plant. The total sulphur present in barley has been determined by various chemists with very different results, probably depending on the method employed. Sorby, by boiling the fresh substance in strong nitric acid, obtained 0.040 and 0.066 per cent. of sulphur in two specimens of dry barley grain; and 0.191 and 0.390 per cent. in dry barley straw. Way, by solution in strong nitric acid, neutralisation with soda, and incineration, obtained 0.74-3.53 per cent. of sulphur (mean 1.68), in various specimens of air-dry barley grain; and 0.54-1.56 (mean 1.07) in barley straw. E. Wolff found 0.16 per cent. of sulphur in dry grain, and 0.10 per cent. in dry straw.

The difference between the maximum and minimum proportions of each ash constituent, as shown in the table, is far greater than would occur in barley under ordinary culture; the ashes which chemists have analysed have, indeed, frequently been obtained from experimental field crops grown under exaggerated conditions of manuring. The influence of manures on the composition of barley will be considered presently.

The chemical life-history of barley, as shown by its composition in various stages of growth, has been investigated by Fittbogen (*2nd Suppl.* 123), whose experiments were conducted in pots; and also by Scheven (*J. pr. Chem.* lxxviii. 193), and E. Wolff (*Mitth. aus Hohenheim*, 1860, 221, 230), both of whom operated on ordinary field crops. The following is a summary of Scheven's results:—

The experimental crop was harvested at five periods: (1) June 28, thirty-four days after sowing; the fourth leaf generally developed. (2) July 17; full bloom. (3) July 30; under leaves withered, ears beginning to fill. (4) August 8; leaves mostly withered, ears green. (5) August 21; fully ripe. Omitting the fourth period, the results of which are rather abnormal, the composition of the whole plant varied, as shown on p. 146.

The percentage of water, albuminoids, and ash steadily diminishes as the plant matures, while the carbo-hydrates ~~as~~ steadily increase. Fibre and fat (chiefly waxy matter) attain their greatest proportion at the time of blossom, and afterwards diminish. Turning now to the rate of assimilation by the crop, as shown in its composition per hectare, we see that but little of nitrogen and ash constituents is taken up before blooming, though the amount of carbonaceous matter continues rapidly to

	Percentage composition of dry substance				Kilos per hectare			
	I	II	III	V	I	II	III	V
Albuminoïds . . .	19.38	10.92	9.39	8.17	277	547	568	589
Fat	3.45	3.89	2.27	1.54	49	195	137	97
Carbo-hydrates . . .	37.59	40.00	44.97	50.48	536	2005	2723	3630
Fibre	27.61	37.71	36.71	33.80	394	1890	2223	2436
Ash	11.97	7.49	6.67	6.21	171	375	404	448
Water (in fresh) . .	84.25	74.15	69.28	42.11	7633	14377	13656	6243
Dry substance . . .	15.75	25.85	30.72	57.89	1427	5012	6055	7209

increase. A greater proportion of hydrogen and oxygen is assimilated, in relation to the carbon, in the latter stages of growth, starch instead of albuminoïds being produced.

	Carbon	Hydrogen	Oxygen
Period I.	100	13.4	72.8
" II.	100	12.3	84.9
" III.	100	17.8	165.5
" V.	100	19.1	156.9

Assimilation was most active just before blooming; in the nineteen days between the periods I. and II., half of the total dry matter of the crop was assimilated.

Scheven examined separately the stem, leaf, and ear at the periods above mentioned: the percentage composition of the dry matter was as follows:—

	Stem			Leaf			Ear		
	II	III	V	II	III	V	II	III	V
Albuminoïds . . .	4.89	4.44	3.48	15.83	9.99	6.22	11.65	11.93	14.08
Fat	3.06	1.94	.92	5.71	3.72	2.98	2.47	1.33	1.23
Carbo-hydrates . .	10.48	43.37	31.78	37.60	38.72	35.75	48.77	56.83	68.33
Fibre	15.84	45.07	57.25	30.62	36.65	44.77	32.52	24.81	10.99
Ash	5.73	5.18	6.57	10.24	10.92	10.28	4.59	5.00	5.37
Water (in fresh)	75.70	71.31	55.49	73.76	66.47	17.12	69.11	63.57	32.50
Dry matter, in kiloes per hectare	2216	2763	2534	1881	1252	1237	914	2039	3435

The leaf is seen to contain far more nitrogen, fat, and ash than the stem. Nitrogen and fat diminish in both stem and leaf as the crop matures, while fibre increases. A large amount of the nitrogen and ash constituents of the leaf pass apparently into the ear as the grain matures. The proportion of nitrogen, and of carbo-hydrates, increases in the ear during ripening, while the fibre diminishes; the changes are thus nearly the reverse of those occurring in the leaf and stem.

The ash of the entire barley crop varied in composition during growth as follows:—

	In 100 parts					In kilos per hectare				
	I	II	III	IV	V	I	II	III	IV	V
Potash	39.12	39.10	30.94	22.83	19.06	66.3	146.6	125.0	101.1	94.1
Soda	1.30	.72	.89	1.31	2.20	2.2	2.7	3.6	5.8	10.5
Lime	8.99	6.70	5.91	4.43	3.51	15.3	25.1	21.9	19.6	16.8
Magnesia	2.86	2.72	2.81	3.30	1.81	4.9	10.2	15.4	14.6	8.7
Ferric oxide56	.24	.30	.19	.27	1.0	.9	1.2	.8	1.4
Phosphoric acid . .	12.19	10.64	9.85	12.22	11.25	20.8	39.9	39.8	54.1	53.8
Sulphuric acid . . .	4.49	3.62	3.90	3.15	2.87	7.7	13.6	16.8	14.0	13.7
Silica	28.81	35.23	43.94	50.70	57.18	49.3	132.1	177.5	224.5	273.3
Chlorine	2.14	1.43	1.51	2.56	2.41	3.6	5.4	6.1	11.4	11.5
Ash in dry	11.97	7.49	6.67	6.99	6.21	170.8	375.3	406.8	443.4	478.1

The whole of the potash required by the plant is taken up at a very early stage; indeed, after blooming, the total amount of potash in the crop, as shown by the second half of the table, seems to have considerably diminished. The assimilation of phosphoric acid is more gradual, and continues to a comparatively late stage of growth. The ash constituent, which exhibits the greatest development in quantity, both relative and absolute, is silica; it forms at last more than half the total ash.

Scheven further determined what proportion of each ash constituent existed in a soluble state in the fresh plant; this he did by extracting the finely divided plant with cold water, and then analysing the ash obtained from the extract. The silica of the plant proved almost insoluble in cold water. Of chlorine, more was found in the extract in the last four periods of growth than in the ash of the whole plant, the excess ranging from 27 to 87 per cent.; the chlorides in the ash of the whole plant evidently suffered loss from the action of silica at a high temperature. Omitting the silica and chlorine, 88 per cent. of the other ash constituents existed in a soluble form at the first stage of the experiment; this proportion was reduced to about 56 per cent. by the fourth period, but rose to 75 per cent. when the plant was fully ripe. This great increase in the solubility of the ash constituent, when the stem and leaves had become withered and ceased to exercise any living function, is very remarkable. Phosphoric acid and magnesia showed the greatest diminution in solubility as maturity advanced, but even here the solubility rose again in the last period. The watery extract contained much less sulphuric acid than was found in the ash derived from it. Sulphur compounds were evidently converted into sulphates during the ignition. The ash of the watery extract was also rich in carbonates, which reached their maximum in the second stage; no carbonates were found in the ash of the whole plant, save a small quantity in the first period, the silica displacing the carbonic acid during ignition.

The capacity of any crop for obtaining the various kinds of food which it requires from the soil and atmosphere, on a knowledge of which its economic treatment by the farmer depends, can be ascertained only by careful and long-continued experiments in the field. For information on this head regarding barley we turn to the experiments of Lawes and Gilbert at Rothamsted (*Jour. Roy. Agri. Soc.*, 1873, 89, 275). Chevalier barley has been grown continuously on their experimental field since 1852, the whole of the crop being annually removed from the land. The average produce obtained per acre during the first twenty years on a few of the more characteristic plots is shown in the following table:—

Manures per acre	Dressed corn	Straw	Total produce	Corn to 100 straw	Weight per bushel of dressed corn	Produce of second 10 years over or under first 10 years
	bushels	cwt.	lbs.		lbs.	percent.
No manure	20	11½	2454	86·6	52·3	— 23·6
Mixed cinereals	27½	14½	3162	96·4	53·4	— 20·2
Ammonium salts 200 lbs.	32½	18½	3019	89·2	52·1	— 0·7
Ammonium salts 200 lbs. with alkali-salts	35	20½	4317	86·3	52·8	— 5·3
Ammonium salts 200 lbs. with super-phosphate	47	27½	5760	86·3	53·6	+ 2·7
Ammonium salts 200 lbs. with mixed cinereals	46½	28½	5817	83·2	54·0	— 3
Rape cake (mean 1300 lbs.)	45½	26½	5571	87·3	53·8	—
Farmyard manure, 14 tons	48½	28½	6033	88·5	54·3	+ 14·8

The alkali-salts employed as manure consist of the sulphates of potassium, sodium, and magnesium. The mixed cinereal manure is composed of alkali-salts and super-phosphate. The ammonium salts are a mixture of equal parts sulphate and chloride.

The results quoted above teach us that with barley, as with the other cereals, the ordinary supply of combined nitrogen from the atmosphere is quite insufficient for vigorous growth, and that to maintain crops of average luxuriance, nitrogenous manures are indispensable. The atmospheric supply of carbon is, on the other hand, quite sufficient for the crop. We learn, further, the great effect of phosphates on the crop, and the small effect of alkali-salts, resulting, doubtless, from the greater capacity of the crop for appropriating soil potash than for appropriating soil phosphoric acid. With wheat, alkali-salts, applied with phosphates and ammonia, produce a much

greater effect than with barley. Phosphatic manures favour the early ripening of barley when applied to land in fair condition.

Barley has apparently a distinctly greater power of appropriating soil nitrogen than wheat; this is shown by the greater produce of barley crops receiving no nitrogen, the greater return for the same quantity of nitrogen supplied in manure (*2nd Suppl.*, 780), and the greater use made by barley of the residues left in the soil from previous manuring. With barley, as with wheat, nitrates yield a somewhat better return than ammonium salts supplying the same quantity of nitrogen. The nitrogen of rape cake, existing in the form of albuminoids, is nearly equal in manurial value to the nitrogen of ammonia, 127 parts of nitrogen supplied as rape cake being equal in effect to 100 supplied as ammonia, when both manures are applied with cinereals. The nitrogen of farm-yard manure has, on the other hand, a far lower value than the nitrogen of ammonia, dung containing about 200 lbs. of nitrogen producing a crop little larger than that yielded by 41 lbs. of nitrogen applied as ammonium salts, with superphosphate.

Barley has shorter roots than wheat or rye, but is shown by the Rothamsted experiments to have a great power of collecting food from the surface soil. This power, conjoined with its faculty of early ripening, makes it an extremely valuable crop for many soils and climates.

For the influence of manures and season upon the composition of barley, we must refer again to the long-continued Rothamsted experiments. The following table shows the percentage of nitrogen in dry barley grain and straw grown under different conditions of manuring in the years 1852-57:—

Manures per acre	Nitrogen in dry grain			Nitrogen in dry straw		
	Highest centage	Lowest centage	Average of six years	Highest per- centage	Lowest per- centage	Average of six years
Cinereal manures only	1.73	1.41	1.57			.46
Cinereals, and 200 lbs. ammonium salts	1.81	1.48	1.70			.49
Cinereals, and 400 lbs. ammonium salts	2.14	1.84	2.00			.53
Cinereals, and 2,000 lbs. rape cake . .	2.08	1.76	1.88			.53

The ammonium salts supplied respectively 41 lbs. and 82 lbs. of nitrogen per acre, the rape cake about 95 lbs. It is seen that when nitrogenous manures are employed, the proportion of nitrogen both in grain and straw is considerably increased, the effect of ammonium salts being especially marked. The percentage of nitrogen in barley is more influenced by the amount of nitrogenous food at its disposal than is the case with either wheat or oats.

The next table shows the influence of manure on the percentage of ash yielded by dry barley grain and straw; the results given are now published for the first time, by the kind permission of Messrs. Lawes and Gilbert:—

Percentage of Ash in dry Barley Grain

	Highest percentage in twenty years	Lowest percentage in twenty years	Average of first ten years	Average of second ten years	Average of twenty years 1852-71
Ammonium salts	2.48	2.01	2.32	2.19	2.25
No manure	2.73	2.39	2.51	2.53	2.52
Mixed cinereals	2.81	2.41	2.62	2.51	2.56
Cinereals and ammonium salts . .	2.66	2.27	2.47	2.51	2.49
Farmyard manure	2.87	2.27	2.63	2.67	2.65

Percentage of Ash in dry Barley Straw

Ammonium salts	6.42	3.67	4.76	4.67	4.71
No manure	6.17	4.23	5.21	5.18	5.19
Mixed cinereals	6.96	5.09	5.67	5.60	5.88
Cinereals and ammonium salts . .	6.70	4.19	5.38	5.71	5.54
Farmyard manure	7.55	4.53	5.50	6.18	5.84

The percentage of ash in the plant is clearly influenced by the extent of the supply furnished by the soil. The plot uniformly manured with ammonium salts, but receiving no ash constituents during twenty years, is the one where exhaustion of cinereal matter has been greatest; here the proportion of ash is least both in corn and straw, and this proportion has diminished during the experiment, being less in the second ten years than in the first. The plot receiving cinereal manures only, and that supplied with farmyard manure, are those in which the supply of cinereal food is most excessive; here the proportion of ash in corn and straw is at its maximum, and the proportion has, in most cases, increased during the course of the experiment. The quantity of ash in the straw is plainly more subject to variation than that in the grain. The differences due to season, as shown by the difference between the highest and lowest percentages, are greater than those due to the character of the manures employed.

When we next turn to the composition of the ash, we find that it is influenced to some extent by the nature of the ash constituents at the disposal of the crop. In the following tables, some selected analyses are given of the ash of barley grain and straw, grown at Rothamsted, in the course of the continuous experiments with this crop. The analyses are by R. Richter, and are now published by Messrs. Lawes and Gilbert's kind permission:—

Percentage Composition of the Ash of Barley Grain variously Manured.

	1856			1871		
	Ammonium salts alone	No manure	Farmyard manure	Ammonium salts alone	No manure	Farmyard manure
Pure ash in dry corn . . .	2.25	2.35	4.48	2.31	2.60	2.85
Potash	24.73	25.68	23.75	29.75	29.52	29.37
Soda	1.03	.77	.22	2.23	1.32	.40
Lime	4.35	3.75	3.87	3.40	2.94	2.23
Magnesia	9.09	8.67	8.75	8.21	7.70	7.78
Ferric oxide78	.82	.85	.36	.60	.31
Phosphoric acid	39.74	40.54	41.98	31.75	34.46	36.89
Sulphuric acid	2.27	2.18	1.49	2.26	2.27	1.66
Chlorine04	.03	.03	3.69	1.73	.31
Silica	17.98	17.57	19.07	19.18	19.86	21.12

Percentage Composition of the Ash of Barley Straw variously Manured.

	3.16	1.29	4.68	5.42	5.95	7.42
Pure ash in dry straw . . .	3.16	1.29	4.68	5.42	5.95	7.42
Potash	11.06	12.23	13.44	17.35	19.79	29.65
Soda	3.64	2.48	1.03	13.42	6.08	2.65
Lime	11.83	12.30	10.61	10.05	10.43	6.62
Magnesia	2.61	2.44	1.97	2.06	2.04	1.31
Ferric oxide	1.45	2.91	1.23	.36	.81	.31
Phosphoric acid	5.80	6.07	6.25	1.89	3.30	3.79
Sulphuric acid	4.75	4.70	3.20	4.57	5.75	3.30
Chlorine	1.98	1.32	.98	15.31	7.23	12.10
Silica	57.32	55.84	60.51	38.50	46.20	43.10

The analyses selected relate to two years, which are especially characterised by a low and high proportion of ash in the crop; the results thus illustrate the effects of season as well as that of manure. Looking first at the composition of the ash in 1871, the twentieth year of the experiment, we have before us the effect both of great exhaustion and abundant supply of cinereal food. On the plots receiving respectively ammonium salts alone, and no manure, the soil has been greatly exhausted of ash constituents, especially on the first-named plot; while the plot manured with farmyard manure has received annually far more of ash constituents than was removed in the produce. The percentage of total ash, both in corn and straw, is seen

to vary with the supply furnished by the soil, the percentage in the grain being more uniform than that in the straw. The detailed composition of the grain ashes is, however, very similar, notwithstanding the wide difference in the character of the manures. Phosphoric acid is the only ingredient of the grain ash which is found in distinctly smaller proportion in the produce of the exhausted land. The ash of the straw shows the same evidence of exhaustion of phosphoric acid on those plots where none has been applied, but besides this exhibits a striking diminution of potash, and substitution of soda, where alkalis have been withheld from the crop. In both straw and grain, a large increase of chlorine is observed, where chloride of ammonium has been employed; in the grain the chlorine is probably confined to the adhering chaff. It appears on the whole, that the ash of barley grain is affected more in amount than in composition by a large or small supply of ash constituents in the soil; phosphoric acid, in this instance before us, is the only ingredient distinctly altered in proportion. The ash of the straw is much more variable, both in amount and composition, the proportion of alkalis, chlorine, and phosphoric acid being greatly dependent on the supply afforded by the soil.

The ash analyses of 1856 belong to a much earlier stage of the experiment, when both the exhaustion and accumulation of ash constituents was far smaller than in 1871; comparing these analyses, however, among themselves, differences will be perceived, similar to those already noticed, though smaller in amount. When, however, we contrast the results of 1856 with those of 1871, the differences observed are very striking. The total ash in 1856 is smaller than in 1871, and contains a smaller proportion of alkalis and chlorine, and a larger proportion of lime, magnesia, and phosphoric acid. In the grain these differences are confined to moderate limits, but in the straw they become extremely large, the alkalis in 1856 being only one half, and the phosphoric acid about double that present in 1871, while the chlorine is affected to an even greater extent. These striking variations are due to differences in the climate of the two seasons, 1856 and 1871, and demand a brief consideration.

Certain general rules govern the proportion of ash which will be found in crops grown in different seasons. Other things being equal, the proportion of ash will be lower as the crop is larger, and more perfectly matured. In a fine season a much larger amount of carbon is assimilated by the crop than in a bad season, and the percentage of ash is consequently diminished. Thus, as a rule, well-matured grain having a high weight per bushel, will yield less ash than grain of an inferior season, having a lower weight per bushel. This general rule may, however, be entirely overridden by special circumstances connected with the season. Barley appears especially subject to such influences, and the twenty years' experiments at Rothamsted do not always show a low ash associated with a high weight per bushel, but frequently the reverse, and a most striking example of this is afforded by the results obtained in 1856 and 1871. In 1856 the total crop produced by farmyard manure was scarcely more than half that yielded in 1871, the weight per bushel of the corn was only 47.1 lbs., while in 1871 it reached 56.6 lbs.; 1856 was thus pre-eminently a bad season, while 1871 was above the average. Yet we have already seen that 1856 was a year of minimum ash contents, while in 1871 the ash was at a maximum, a result directly contrary to the general principle stated above.

A study of the Rothamsted results, together with the meteorology of the respective seasons, has led the writer to conclude that the kind of weather experienced at two epochs of the life of the crop has a preponderating effect on the percentage of ash in the produce. If an excess of rain occurs in the middle of summer, when the green crop is at its greatest bulk, and transpiration of water most active, a considerable amount of soluble ash constituents will be taken from the soil by the crop. If this excess of rain is followed by dry weather as the straw begins to wither and the grain ripens, these soluble ash constituents will be retained by the crop, and the produce will yield a maximum percentage of ash, rich in alkalis and chlorine. Such a season was that of 1871. If, on the contrary, the middle of summer is dry, the amount of ash constituents taken up by the crop will be smaller; and if the ripening and harvest period are wet, a considerable proportion of the chlorides and soluble alkali salts are apparently washed out from the straw and the chaff of the grain, leaving a low percentage of ash rich in silica. Such a wet harvest was that of 1856. These general conclusions need the test of a wider experience; they explain, however, the results observed, and, as far as the washing out of soluble salts from the dead straw and chaff during a wet harvest is concerned, are in accordance with the observations of Scheven already noticed.

An average crop of barley of 40 bushels of corn, at 52 lbs. per bushel, and 2447 lbs. of straw (85 corn to 100 straw), will remove from the land, 125 lbs. per acre, about the following quantities of nitrogen and ash constituents:—

	Nitro- gen	K ² O	Na ² O	CaO	MgO	Fe ² O ³	P ² O ⁵	SO ³	Cl	SiO ²	Total ash
Grain	35	9.8	1.0	1.3	4.0	.4	16.2	.8	.4	12.0	46
Straw	12	21.6	4.2	6.5	2.5	.8	4.4	4.0	3.2	51.5	100
Total	47	31.4	5.2	9.8	6.5	1.2	20.6	4.8	3.6	63.5	146

BARWOOD. See BAPHIA (p. 140).

R. W.

BARYTA-GREEN. To prepare this pigment, 2 parts of finely powdered manganese dioxide are gradually introduced into a fused mixture of 2 parts of potassium hydrate and 1 part of potassium chlorate, and the mass is heated to low redness, left to cool, powdered, treated with cold water, and filtered. Barium nitrate is then added to the filtrate, and the violet barium manganate is washed, mixed with $\frac{1}{2}$ to 1 part of barium hydrate, and heated to low redness in a copper basin, till it assumes a pure green colour. Lastly, it is powdered and treated with water to remove free barium hydrate.

BARYTA-MICA. This mineral occurs in the Habachthal in Salzburg. It crystallises in the rhombic system, the faces ∞P and $0P$ being distinct, and the latter face having a pearly lustre. Cleavage very distinct, parallel to $0P$, by which it can be obtained in very thin flexible laminæ. The mineral is mono-axial, and is generally analogous to potash-mica. Colour white; colourless in thin laminæ. Hardness 1.5; sp. gr. 2.83 at 10° C. Easily fusible before the blowpipe to a white enamel. On boiling with sulphuric and hydrochloric acids it is slightly attacked but not decomposed. Analysis gave:—

SiO ² .	Al ² O ³ .	FeO.	MnO.	MgO.	BaO.	CaO.	K ² O.	H ² O.
49.44	26.05	2.02	0.29	3.03	5.76	1.81	7.54	4.24 = 100.18.

Not the slightest trace of sodium could be detected, even by the spectroscope (Sandberger, *Jahrb. f. Min.* 1875, p. 625):

BASALT. On the Basalts of Styria, see G. Untchj (*Jahrb. f. Min.* 1873, 321; *Chem. Soc. J.* [2], xi. 1115).

On the occurrence of Zeolites in the Basalt of the Lämperichkoff at Asbach, see A. Weiss (*Jahrb. f. Min.* 1873, 319; *Chem. Soc. J.* [2], xi. 1116).

On the Basalt and Hydrotachylite of Rossdorf, Darmstadt, see Peterson (*J. pr. Chem.* [2], vii. 152; *Chem. Soc. J.* [2], xi. 1211).

On the Basalt of the Schiffeberg: Winther (*Jahrb. f. Min.* 1877, p. 102).

On the action of a Basaltic Magma in the state of Igneous Fusion on crystals enclosed in rocks and minerals, as observed in the lavas and basalts of the Lower Rhine, see J. Lehmann (*Jahrb. f. Min.* 1874, 431).

Titanium and Vanadium in Basalts.—Titanium occurs in the basalts of Clermont Ferrand, Auvergne, in larger proportion than in any basalt hitherto examined. The lowest percentage obtained in ten analyses was 0.707, and the highest 2.378, the mean being 1.501. The titanium is best determined as follows:—The basalt is fused with sodium carbonate, the cooled mass dissolved in hydrochloric acid, the solution evaporated to dryness, and the silicic acid dehydrated as usual. The whole is then boiled with dilute acid, and the silica filtered off: both precipitate and filtrate contain titanium. The silica is ignited, and then treated with warm oil of vitriol for several hours. The pure silica is left insoluble after this operation, and the titanium is precipitated from the solution by ammonia. The original filtrate from the silica is boiled with sodium sulphate, sulphuric acid, and sodium thiosulphate. The impure titanic oxide is gently ignited, then mixed with that obtained from the silica, and the whole is digested in a sealed tube with warm concentrated hydrochloric acid. The residue is titanic oxide.

The percentage of vanadic oxide in the same basalts varied from 0.006 to 0.023, the mean being 0.014 (V. Roussel, *Compt. rend.* lxxvii. 1102).

BASES. On the combining proportions of Bases and Acids, see ACIDS (p. 37).

On the division of a Base between two Acids, see CHEMICAL ACTION (2nd Suppl. 286).

BAUMSTA. See 2nd Suppl. 125.

BEECH. *Fagus sylvatica.*—Beech leaves yield a fragrant decoction, and 100 parts of the dry leaves give 20.8 parts of a fluid extract, which, when burned, yields 2.44 parts of ash containing a notable proportion of manganese. The total percentage

of ash from the dried leaves is 4.52, of which 2 parts are soluble in water, and 2.52 parts insoluble (Wanklyn, *Chem. News*, xxiii. 186).

Beech-blight.—The beech trees in Westphalia were attacked in 1872 by a new form of blight, which, commencing on the bark, finally covers the tree with a snow-white down, producing sickness, and sometimes death. The microscope shows this blight to consist of fine threads, among which occurs a small insect, apparently an undescribed species. These threads, which are secreted by the insect, consist of wax, which has a melting point of 78°–80°, and contains carbon 81.39 per cent., hydrogen 13.58, oxygen 5.03. Both composition and melting point are very near to those of Chinese wax. The wax was partly saponified by potash, and on shaking up the resulting soap with ether, a substance was obtained melting at 49°–51.5°, solidifying at 50°–48°, and containing carbon 76.21, hydrogen 12.24, oxygen 11.55. The soap yielded an acid melting at 51°–53°, solidifying at 50°–49°, and containing carbon 77.88, hydrogen 12.31, oxygen 9.81. The unsaponified portion, which must have been richer in carbon, melted at 140°–145° (J. König, *Landw. Versuchs-Stationen*, xvi. 198).

BEECH WAX. See WAX.

Manufacture of Unalterable Beer.—The liability of beer to turn sour, rropy, &c., is due to the presence of special ferments derived from the air, and from the materials used. By boiling the infusion of malt and hops, cooling out of contact with air, and fermenting with pure yeast in vessels to which only carbonic acid or pure air is admitted, a beer is produced of superior quality, which may be preserved without trouble for any time. Even a partial adoption of these precautions is attended with valuable results. In preparing pure yeast to start with, advantage may be taken of the fact that oxygen favours the growth of true yeast, but hinders the propagation of the other ferments. Pure yeast being obtained, the beer is afterwards fermented in an atmosphere nearly destitute of oxygen, as its quality is thereby improved. Pure yeast when kept in pure air undergoes no change, even at summer temperatures. The *Mycoderma vini* does not become changed into beer-yeast on submersion in a nutritive fluid; under these circumstances it acts as an alcoholic ment, but does not propagate itself (Pasteur, *Compt. rend.* lxxvii. 1140).

Hirschberg (*Arch. Pharm.* [2], cl. 45) finds that the addition of a small quantity of boric acid to beer retards its tendency to become 'hard.'

On the manufacture of Beer from Beetroot, see F. Coules (*Dingl. pol. J.* cxx. 478; *Chem. Soc. J.* [2], xii. 725).

Detection of Foreign Bitters in Beer.—A. Dragendorff (*Arch. Pharm.* [3], ii. 295; iv. 380), has examined the reactions of the following substances, used more or less frequently to give bitterness to beer: Quassia, *Ledum palustre*, absintho, *Mentha trifoliata*, *Cnicus benedictus*, *Erythraea Centaurium*, gentian, willow-bark, aloes, picric acid, colocynth, *Cocculus indicus*, colchicum seeds, *Daphne Mezereum*, *Capsicum annum*, *Belladonna*, *Hyoscyamus*, *Nux vomica*, and juniper berries. The following are the general methods of detection employed:—

I. 600–1,000 c.c. of beer are evaporated to a syrupy consistence on the water-bath, and then treated with 3–4 volumes of alcohol, as free as possible from fusel-oil, and the mixture is allowed to stand twenty-four hours. The whole is then filtered; the alcohol is distilled off from the filtrate; and the residual liquid is again filtered after standing for 12–20 hours in the cold. A few drops of dilute sulphuric acid are then added; the whole is agitated with petroleum ether; and the supernatant petroleum layer is washed with water, filtered through dry filter-paper so as to remove the last traces of water, and evaporated to dryness on several watch-glasses by spontaneous evaporation. The aqueous acid liquor is then agitated with benzene and with chloroform, and then again with benzene, after addition of ammonia to liberate alkaloïds; salicin from willow-bark is extracted by agitating the aqueous liquor with amyllic alcohol.

II. 600–1,000 cc. are heated till most of the dissolved carbonic acid is driven off; after cooling, basic lead acetate is added, till no further precipitate is formed; after standing for some hours the whole is filtered; and diluted sulphuric acid is then added to throw down the excess of lead; if the filtrate has a harsh or bitter taste, the beer is suspicious. The whole is then evaporated on the water-bath (after neutralisation by ammonia) as quickly as possible, until only 180–200 c.c. are left, and then treated with benzene, petroleum ether, and chloroform, as in method I.

Normal beer, examined by method I., gives the following results:—The petroleum ether extract contains: (1) an amorphous, slightly bitter substance, soluble in ether and alcohol, and partially soluble in water; (2) a substance which precipitates basic lead acetate; (3) a substance which becomes red with Fröbde's reagent (sodium-

thiosulphate), and (4) one which becomes red with sulphuric acid and sugar. The benzene extract contains the same substances, and is more bitter; in addition, it contains (5) a body which becomes dark brown on treatment with sulphuric acid; and (6) a substance which precipitates tannin. The chloroform extract contains substances 1, 2, 5, and 6, in some instances in larger proportions; also (7) traces of a body precipitable by potassium iodide and phosphomolybdic acid; (8) a body which reduces ammoniacal silver nitrate; and (9) a body crystallisable from ether, and difficultly soluble in alcohol. Of these substances, 2, 3, and 6 come from the hops, 1 from hops and malt together, 4, 5, 7, and 8 from malt, and 9 is formed from malt in fermentation.

Examined by Method II., normal beer should give next to no extract with petroleum-ether; but little benzene extract, and that not bitter, and not precipitating gold, or reducing it on warming, and only an inconsiderable chloroform extract. Hence substances 2, 3, 4, 6, and 8, are removed by the lead acetate; consequently, when any adulterant not precipitable by this agent is sought for, Method II. should be used.

The following table exhibits the characters of the extracts obtained by the aid of these several solvents from the plants and vegetable products above mentioned; the reactions observed with the bitter ingredients thus isolated, when treated with the following substances: chloride of gold; tannin; basic lead acetate; ammoniacal silver solution; concentrated sulphuric acid; Fröhde's reagent; sulphuric acid and sugar; sulphuric acid with 5 proportions of water, $H^2SO_4 + 5H^2O$, on warming; warm dilute sulphuric acid; caustic potash solution; warm ferric chloride; also their physical properties, e.g. crystalline form, taste, &c. 600 cc. of beer being taken for examination, 0.0005 gram of atropine (0.06 gram of belladonna leaves); the same quantity of hyoscyamine (0.25 gram of henbane); 0.0003 of strychnine, and 0.0005 gram of brucine (0.03 gram of nux vomica), can be detected by the methods described.

EXTRACT FROM ACID LIQUOR.

Residue from Petroleum.

- (a) Amorphous, first becomes brown, then violet, and soon red-violet, with sulphuric acid. *Traces of Absinthin.*
- (b) Amorphous, colourless, sharp-tasting, and rubefacient; coloured brown-red with sulphuric acid. *Traces of Capsicin.*
- (c) Amorphous, green, becoming red with sulphuric acid and sugar; no precipitate with ammoniacal silver solution. *Juniper-berry Resin.*
- (d) Crystalline, yellow, becoming blood-red with potassium cyanide. *Picric Acid.*

Residue from Benzene.

- [A] Crystalline, not bitter; becomes purple-red with potash, and red, changing to orange, with sulphuric acid. *Aloëtin.*
- [B] Amorphous.
 - (a) No precipitate with gold chloride when the residue is dissolved in water:
 - (1) Tannin gives no precipitate: residue sharp-tasting:
 - [a] Sulphuric acid colours the liquid red-brown. *Capsicin.*
 - [β] Sulphuric acid colours the liquid brown. *Daphne Bitter.*
 - (2) Tannin precipitates the aqueous solution; residue bitter, or bitterish:
 - [I] Basic lead acetate causes slight turbidity; sulphuric acid and sugar hardly redden the solution.
 - aa. Ferric chloride gives brown-green tint on warming the aqueous solution; slightly bitterish. *Gentian Leaves.*
 - bb. Ferric chloride gives brown tint on warming; peculiar taste, intolerably bitter. *Quassin.*
 - [II] Basic lead acetate gives a copious precipitate; sulphuric acid and sugar quickly give cherry-red tint; weakly bitterish. *Cucitin.*
 - (b) Aqueous solution of residue does not act on gold chloride in the cold, but reduces on warming.
 - [a] Slight precipitate with tannin; does not reduce ammoniacal silver solution; heated with dilute sulphuric acid, it gives the odour of ericinol; Fröhde's reagent colours it black-brown, sulphuric acid and sugar a beautiful red. *Ledum Bitter.*
 - [β] Precipitate with tannin; ammoniacal silver reduced; heated with dilute sulphuric acid, it gives a slight odour of menyanthol. *Trifolium Bitter.*
 - (c) Aqueous solution of residue precipitates gold chloride in the cold, but

- does not reduce it on heating; with $\text{SO}^4\text{H}^2 + 5\text{H}^2\text{O}$ gives a slight odour of benzoic acid. *Centaury Bitter.*
- (d) Aqueous solution of residue precipitates gold chloride in the cold, and reduces it on warming; sulphuric acid dissolves it to a brown tint at first, soon turning violet, and becoming a beautiful violet on addition of water; hydrochloric acid of sp. gr. 1.185 colours it first green, then a beautiful blue. *Absinthin.*

Residue from Chloroform.

- [A] No precipitate and no reduction with gold chloride:
- (a) Tannin gives no precipitate; sharp taste; vesicating; sulphuric acid colours it dark brown-red. *Capsicin.*
- (b) Tannin gives a precipitate.
- [a] Basic lead acetate gives considerable precipitate; heated with dilute sulphuric acid, it becomes turbid, then brown-red, and gives a faint odour of benzoic acid. *Cnicin.*
- [β] Basic lead acetate gives little or no precipitate.
- I. Sulphuric acid gives a brown colour:
- aa. Residue very bitter. *Quassia.*
- bb. Residue bitterish. *Gentian.*
- cc. Residue sharp-tasting. *Daphne bitter.*

II. Sulphuric acid gives a slight yellow tint or no colour at all. *Colocynth.*

- [B] Gold chloride gives no precipitate in the cold, but is reduced on warming:
- (a) Tannin gives no precipitate:
- [1] Stupifies fish; bitter taste. *Picrotoxin.*
- [2] Tasteless or slightly bitter; potash colours it red-brown. *Aloes.*
- (b) Tannin gives a precipitate:
- [a] Ammoniacal silver reduced; strong odour of menyanthol on heating with dilute sulphuric acid, or Fröhde's reagent. *Menyanthin.*
- [β] Ammoniacal silver not reduced; odour of ericicol with dilute sulphuric acid, or with Fröhde's reagent; beautiful carmine-red on long standing with sulphuric acid and sugar. *Ericolin.*
- [C] Gold chloride gives a precipitate in the cold, and is not reduced on warming; nitric acid gives a violet tint. *Colchicum.*
- Heated with sulphuric acid, it gives an odour like that of clover, then the liquid becomes red, and the smell alters to one resembling benzoic acid. *Centaury Bitter.*
- [D] Gold chloride gives a precipitate in the cold, and reduces on heating; sulphuric acid colours it brown, and gradually dirty violet. *Wormwood Bitter.*

•EXTRACT FROM ALKALINE LIQUOR.

- [I] *Benzene residue.*
- (a) Dilates the pupils of a cat's eye:
- (1) Platinum chloride does not precipitate the aqueous solution; peculiar odour on warming with sulphuric acid. *Atropine.*
- (2) Platinum chloride gives a precipitate when in just the right proportion. *Hyoscyamine.*
- b) Does not dilate the pupil:
- [a] Sulphuric acid solution becomes blue with potassium dichromate or ceric oxide. *Strychnine.*
- [β] Sulphuric acid solution becomes red with nitric oxide. *Brucine.*
- [II] *Amylic alcoholic residue* (examined only when Salicin is to be sought for).
- Heated with sulphuric acid and potassium dichromate, gives a salicylous odour. *Salicin.*

For the detection of picric acid in beer, Vitali (*Gazz. chim. ital.* vi. 466) recommends the use of amyl alcohol. 10 cub. cent. of the beer are agitated with 5 cub. cent. of amyl alcohol, the latter being removed by means of a pipette, filtered and evaporated; a yellow residue indicates picric acid. This is dissolved in a small quantity of water, and divided into four portions, which are severally treated with ammoniacal copper sulphate, potassium cyanide, ammonium hydrosulphide, and potassium nitrate: if picric acid is present, these give the crystalline ammonium

copper picrate, the purple-red isopurpuric and picramic acid, and the yellow crystalline potassium picrate.

On the Detection of Adulterations in Beer, see also Wittstein (*Arch. Pharm.* [3], v. 25; *Chem. Soc. Jour.* 1876, i. 767).

On the Composition of Beers brewed in Basel, see Goppelsroeder (*Dingl. pol. J.* cccvii. 328; *Chem. Soc. Jour.* 1876, i. 768).

On Substitutes for Malt in Brewing (*Surrogatbrauerei*), see Hänemann (*Dingl. pol. J.* cccviii. 345; *Chem. Soc. Jour.* 1876, i. 807).

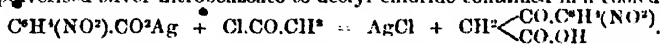
BEHENIC or **BENIC ACID**. This acid, or rather its glyceride, has been found by Goldschmidt in the fat oil of black mustard seed (see **MUSTARD**).

BELLADONNA. On the preparation of Atropine from Belladonna leaves, see **ATROPINE** (p. 135).

BENZACETIC or **BENZOYL-ACETIC ACID**, $C^6H^5O^2 = CH^2 \begin{smallmatrix} CO.C^6H^5 \\ CO.OH \end{smallmatrix}$.

The metanitro- and metamido-derivatives of this (at present unknown) acid have been prepared and examined by L. Liebermann (*Deut. Chem. Ges. Ber.* x. 861).

The *nitro-acid*, $C^6H^5NO^3 = CH^2 \begin{smallmatrix} CO.C^6H^5(NO^2) \\ CO.OH \end{smallmatrix}$, is obtained by gradually adding finely pulverised silver nitrobenzoate to acetyl chloride contained in a cooled vessel:



It is necessary to use an excess of acetyl chloride, since, if the two bodies are mixed in equivalent proportions, the quantity of liquid present will not be sufficient to ensure complete mixture. On pouring the product, with stirring, into a large quantity of water, filtering from silver chloride, and evaporating the filtrate in the water-bath, the nitro-acid is obtained in long spicular crystals apparently belonging to the quadratic system. After pressing and drying at 100°, it forms a light, loose, very bulky, crystalline powder.

Metanitrobenzætic acid is easily soluble in alcohol, ether, and hot water, sparingly in cold water. The aqueous solution has a strong acid reaction. When heated in a small glass tube, it melts at 130°–132° (corr.) to a yellowish liquid, and then decomposes, giving off an odour of bitter almonds and forming a crystalline sublimate. When suddenly heated, it detonates somewhat violently. By the action of strong mineral acids it is resolved into acetic and nitrobenzoic acids; by tin and hydrochloric acid into acetic and amidobenzoic acids.

The *lead-salt*, $(C^6H^5NO^3)_2Pb + 2H^2O$, prepared by agitating the acid aqueous solution of the nitro-acid with lead oxide till the acid reaction disappears, and evaporating the filtered liquid, crystallises in thin needle-shaped prisms. The barium and silver salts are very unstable.

Metamido-benzætic acid, $C^6H^5NO^3 = CH^2 \begin{smallmatrix} CO.C^6H^5(NH^2) \\ CO.OH \end{smallmatrix}$, metameric with

hippuric (benzamidacetic) acid, $CH^2 \begin{smallmatrix} NH.CO.C^6H^5 \\ CO.OH \end{smallmatrix}$, and with Foster's acetyl-met-

amidobenzoic acid, $C^6H^5 \begin{smallmatrix} NH.C^6H^5O \\ CO.OH \end{smallmatrix}$ (i.e. 291), is formed by reducing the nitro-acid with ammonium sulphide in alcoholic solution, and may be obtained pure by acidulating the liquid with acetic acid—after expelling the hydrogen sulphide—selecting the last portions which crystallise out, and decolorising them with animal charcoal. It is moderately soluble in water, and decomposes when melted, yielding a crystalline sublimate and a residue melting at 166°, which is so near the melting point of metamidobenzoic acid (165°) as to render it probable that the residue in question actually consists of this acid.

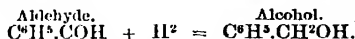
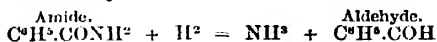
BENZACRYLIC ACID, $C^6H^5O^2$. This name is given by Pfankuch (*J. pr. Chem.* [2], vi. 97) to an acid which he obtained by distilling a mixture of barium benzoate with excess of barium thiocyanate, and treating the liquid portion of the distillate with potash. The free acid crystallises in small glistening needles melting at 101°. It is a stronger acid than benzoic acid, but less stable.

BENZAMIDE, $C^6H^5O.NH^2 = C^6H^5.CONH^2$. On the formation of this compound and benzonitril by heating benzoic acid with thiocyanates, see *2nd. Suppl.* 160. On its crystalline form, see *2nd Suppl.* 129.

Mercury-compound.—The compound, $(C^6H^5O.NH^2)_2Hg$, obtained by dissolving mercuric oxide in aqueous benzamide (i.539), boils without decomposition at 222°–224°. It is decomposed by carbon disulphide and thiocarbonyl at a low temperature,

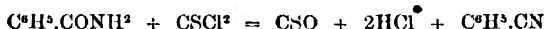
with separation of benzamide and formation of benzonitril, but not of benzoyl-guanidine or benzoyl-urea. The reaction with carbon disulphide is attended with formation of carbon oxysulphide (Oppenheim a. Czarnomsky, *Deut. Chem. Ges. Ber.* vi. 1392).

Conversion into Benzyl alcohol and Benzoic aldehyde.—When a mixture of benzamide with ether and a little water is submitted to the action of nascent hydrogen (evolved by sodium amalgam, not by zinc) benzyl alcohol is formed, together with a small quantity of benzoic aldehyde:



This reaction may perhaps afford a good method of preparing benzyl alcohol, as the yield may amount to more than 30 per cent. of the benzamide employed (Guareschi, *Gazz. chim. ital.* iv. 465).

Reaction with Sulphocarbonyl Chloride, CSCl_2 .—When this compound is heated with benzamide to 150° in sealed tubes, part of it abstracts water from the benzamide, forming benzonitril, together with hydrochloric acid and carbon oxysulphide; while the greater part of the sulphocarbonyl chloride is converted into a mixture of carbon disulphide and carbon tetrachloride, without further action on the benzamide, three-fourths of which indeed remains unattacked:—

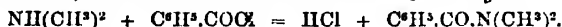


and



At the same time the hydrochloric acid formed in the reaction acts upon the benzamide in such a manner as to produce hydrated dibenzamide, $\text{C}^{12}\text{H}^{13}\text{NO}^4 = \text{NH}(\text{C}^6\text{H}_5\text{O})^2 + 2\text{H}^2\text{O}$, which may, in fact, be formed directly by the action of hydrochloric acid on benzamide (p. 167) (Rathke a. Schäfer, *Liebigs Annalen*, clxix. 107, 111).

Dimethyl-benzamide, $\text{C}^6\text{H}_5\text{CO.N}(\text{CH}^3)^2$, and **Diethyl-benzamide**, $\text{C}^6\text{H}_5\text{CO.N}(\text{C}^2\text{H}_5)^2$, are formed by the action of benzoyl chloride on dimethylamine and diethylamine, both the chloride and the amide being diluted with eight times their volume of ether, to moderate the violence of the action: *e.g.*—

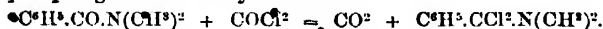


The hydrochloride of the amino formed at the same time is extracted with water, and the ethereal solution is dried over calcium chloride and evaporated.

Diethyl-benzamide is a colourless oil, boiling at 280° – 282° , not miscible with water, soluble in dilute hydrochloric acid, but reprecipitated on addition of water.

Dimethyl-benzamide forms crystals easily soluble in water, melting at 41° – 42° , and boiling at 255° – 257° (uncorrected). Heated with hydrochloric acid to 200° it separates into dimethylammonium chloride and benzoic acid.

Dimethyl-benzamidochloride, $\text{C}^6\text{H}_5\text{NCl}^2 = \text{C}^6\text{H}_5\text{CCl}_2\text{N}(\text{CH}^3)^2$, is formed by the action of liquid phosgene on dimethylbenzamide:



When equal volumes of liquid phosgene and dimethyl-benzamide are enclosed for several hours in a sealed tube, a white crystalline mass is formed, and streams of carbon dioxide escape on opening the tube. The crystals fume in damp air, smell like benzoyl chloride, and decompose readily in contact with water, yielding HCl and dimethyl-benzamide (F. Hallmann, *Deut. Chem. Ges. Ber.* ix. 846).

Dibenzamide, $\text{NH}(\text{C}^6\text{H}_5\text{O})^2$, or $\text{C}^6\text{H}_5\text{CO.NH.CO.C}^6\text{H}_5$, is prepared by slowly adding cyanobenzene (7 parts) to a mixture of strong sulphuric acid (7 parts) and phosphoric anhydride (4 parts); agitating the mixture till it becomes homogeneous; adding water after some hours, and leaving the solution to itself. It then deposits a mass of slender needles, which, after crystallisation from weak spirit, consist of pure dibenzamide. The reaction may be represented by the equation:



but it is uncertain whether the formation of the dibenzamide takes place before or after the addition of water.

Dibenzamide crystallises in long thin colourless needles, which melt at 144° and decompose without subliming at a higher temperature. It dissolves sparingly in boiling water, easily in alcohol, ether, chloroform, and benzene. Its reaction is neutral. Boiled with potash-ley it yields ammonia and potassium benzoate. When agitated with dilute soda-ley in the cold, it forms *sodium-dibenzamide*, $(\text{C}^6\text{H}_5\text{O})^2\text{NNa}$,

which crystallises from water in short prisms containing $\frac{1}{2}$ mol. of water. The aqueous solution of sodiumbenzamide gives precipitates with salts of the heavy metals. The silver compound is a white semi-crystalline body. The mercury, zinc, lead, and copper compounds are curdy precipitates, quickly becoming crystalline (Barth a. Senhofer, *Deut. Chem. Ges. Ber.* ix. 975).

Hydrated Dibenamide, $C^6H^5NO^2 = NH(C^6H^5O)^2 + 2H^2O$, is formed, as already observed (p. 156), by the action of hydrochloric acid on benzamide. It crystallises in transparent plates melting at 99° , moderately soluble in water, soluble also in alcohol, ether, and chloroform. The aqueous solution has an acid reaction. The compound boiled with dilute alkaline carbonates gives off ammonia and yields benzoic acid. The two molecules of water which it contains cannot be expelled without further decomposition (Rathke a. Schäfer, *Liebig's Annalen*, clxix. 107, 111).

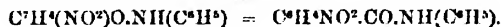
Seleniobenzamide, $C^6H^5NSe = C^6H^5.CSeNH^2$, is formed by the action of hydrogen selenide on a slightly ammoniacal alcoholic solution of benzonitril. It crystallises in large golden-yellow needles. On boiling it with iodine, part of the selenium is removed and a compound is formed, probably having the composition $(C^6H^5CN)^2Se$, analogous to the sulphur compound (1st Suppl. 258) which Hofmann obtained in like manner from thiobenzamide (F. von Dechend, *Deut. Chem. Ges. Ber.* vii. 1273).

BENZANILIDE or **PHENYL-BENZAMIDE**, $C^6H^5NO = C^6H^5O.NH(C^6H^5) = C^6H^5.CO.NH(C^6H^5)$.

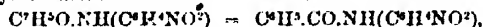
BROMOBENZANILIDE, $C^6H^5Br.CO.NH(C^6H^5)$.—When bromine is added to a solution of benzanilide in glacial acetic acid, bromo-benzanilide is obtained in large thin plates melting at 202° . A small quantity of another compound, probably an isomeride, is formed at the same time (Meinecke, *Deut. Chem. Ges. Ber.* viii. 564).

NITROBENZANILIDES.—The formula, $C^6H^5(NO^2)NO$, represents two isomeric compounds, viz. :—

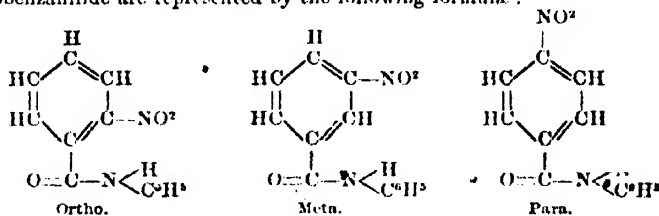
1. Phenylnitrobenzamide or nitrobenzanilide :



2. Nitrophenylbenzamide or benzonitrilanilide :



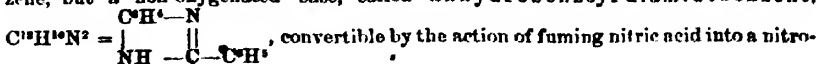
and each of these is susceptible of three modifications, ortho-, meta-, and para-, according to the position occupied by the group NO^2 in the benzene-residue to which it belongs. The benzonitrilanilides have not yet been obtained; the three modifications of nitrobenzanilide are represented by the following formulae :



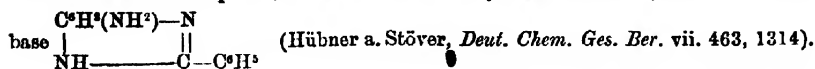
The ortho- and para- modifications are obtained by direct nitration of benzanilide. On dissolving the product, in alcohol, paranitrobenzanilide crystallises out first in small colourless prisms melting at 199° ; and on evaporating the alcoholic mother-liquor to dryness and drenching the residue with chloroform, nearly pure paranitrobenzanilide remains undissolved, while on leaving the chloroform solution to evaporate, and digesting the residue with alcohol, a solution is obtained, from which orthonitrobenzanilide crystallises out, in long light yellow needles very soluble in alcohol and melting at 94° – 95° . The ortho- modification is distinguished from the para- by its greater solubility and lower melting point.

Paranitrobenzanilide, treated with *potash-ley*, yields paranitrilaniline melting at 146° . *Nascent hydrogen* converts paranitrobenzanilide into a benzoyldiamidobenzene (m. p. 125°), which when treated with potash yields para-diamidobenzene melting at 140° .

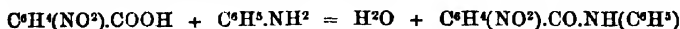
Orthonitrobenzanilide, treated with *potash*, is converted into orthonitrilaniline melting at 67° . With *nascent hydrogen* it yields, not a benzoylated diamidobenzene, but a non-oxygenated base, called anhydrobenzoyl-diamidobenzene,



compound, possessing feeble basic properties, easily soluble in hot glacial acetic acid and alcohol, and crystallising from the latter in groups of small needles melting at 196°. This nitro-compound, heated with tin and hydrochloric acid, yields the bi-acid



Metanitrobenzanilide is prepared by digesting metanitrobenzoic acid with aniline, and crystallising the product from water :



Engler a. Volkshausen (*Deut. Chem. Ges. Ber. viii. 34*). According to Hübner (*ibid.* ix. 774), it is formed, together with the ortho- and para-modifications, by the action of nitric acid on benzanilide, and may be separated by exhausting the crude product with chloroform, which dissolves the *o*- and *m*- derivatives, evaporating the solution, and treating the residue with boiling alcohol, which, as it cools, deposits first the meta-compound.

Metanitrobenzanilide crystallises in colourless leaflets (E. and V.), in yellow needles (Hübner). It dissolves easily in alcohol, ether, or benzene, and melts at 144°, while a higher temperature causes it to sublime in yellowish needles. By reduction with tin and hydrochloric acid, it is converted into *metamidobenzanilide*, $\text{C}^6\text{H}^4(\text{NH}^2).\text{CO.NH}(\text{C}^6\text{H}^5)$.

This amidanilide crystallises from water in long white needles, easily soluble in alcohol and ether, and melting at 114°. When subjected to the further action of reducing agents, it does not yield a non-oxygenated base analogous to that which Stöver obtained from orthonitrobenzanilide.

Hydrochloride of Metamidobenzanilide, $\text{C}^{12}\text{H}^{12}\text{N}^2\text{O}.\text{HCl}$, is obtained in dazzling white needles by evaporation of the solution of the base in hydrochloric acid. The *platinochloride* is a yellow crystalline precipitate. The *sulphate* forms colourless prisms moderately soluble in hot, less soluble in cold water (Engler a. Volkshausen).

Dinitrobenzanilide, $\text{C}^{12}\text{H}^8\text{N}^2\text{O}^2$, = $\text{C}^6\text{H}^4(\text{NO}^2)_2.\text{O.NH}(\text{C}^6\text{H}^5\text{NO}^2)$ = $\text{C}^6\text{H}^4(\text{NO}^2)_2.\text{CO.NH}(\text{C}^6\text{H}^5\text{NO}^2)$, (McHugh, *Deut. Chem. Ges. Ber. vii. 1266*).—This compound is formed by the action of nitrobenzoyl chloride on nitraniline in ethereal solution :



also, according to Engler and Volkshausen, by heating nitrobenzoic acid and paranitraniline in molecular proportions. From the product of the first reaction it separates as a white powder, which may be freed from the nitraniline hydrochloride simultaneously formed, by means of boiling water, which dissolves the latter; the insoluble residue is crystallised from amyl alcohol, in which it is much more soluble than in common alcohol.

Dinitrobenzanilide melts at 187°, and is insoluble in ether, water, and dilute acids. By alcoholic ammonium sulphide it is converted into di-amido-benzanilide, $\text{C}^6\text{H}^4(\text{NH}^2)_2.\text{O.NH}(\text{C}^6\text{H}^5\text{NH}^2)$, which crystallises from alcohol in needles melting at 129°. Nascent hydrogen (from tin and hydrochloric acid) appears to remove all the oxygen, forming a base, which probably has the composition, $\text{C}^{12}\text{H}^{11}\text{N}^3$ = $\text{N}^3\text{H}^3(\text{C}^6\text{H}^4)(\text{C}^6\text{H}^5)$ (McHugh).

Nitrobromobenzanilides.—When bromobenzanilide is treated with fuming nitric acid, the mono-nitro-compound, $\text{C}^6\text{H}^3\text{BrNO}^2.\text{CO.NH}(\text{C}^6\text{H}^5)$, is formed in small yellow laminae melting at 137°–138°, together with a smaller quantity of the dinitro-compound, $\text{C}^6\text{H}^2\text{Br}(\text{NO}^2)_2.\text{CO.NH}(\text{C}^6\text{H}^5)$, melting at 195°–196°.

The mononitro-compound, treated with tin and hydrochloric acid, yields a base apparently having the composition, $\text{C}^6\text{H}^3\text{BrNH}.\text{C} \begin{cases} \text{C}^6\text{H}^5 \\ \text{NHOH} \end{cases}$.

The *hydrochloride* of this base forms slender colourless needles, not very soluble in water. The *nitrate* separates in flocks sparingly soluble in water. The *sulphate* crystallises in very small colourless needles very slightly soluble in water (Meinecke, *Deut. Chem. Ges. Ber. viii. 564*).

C^6H^6 . *Physical Properties*.—According to Adrienzen (*Deut. Chem. Ges. Ber. vi. 441*), benzene from coal tar boils at 80°53'–80°62'; that prepared from benzoic acid at 80°60'–80°67'. The same chemist has made the following determination of the specific gravity of benzene from benzoic acid at various temperatures :

Temp.	Sp. gr.	Temp.	Sp. gr.	Temp.	Sp. gr.
0°	0.90023	30°	0.86891	60°	0.83642
5°	0.89502	35°	0.86362	65°	0.83078
10°	0.88982	40°	0.85829	70°	0.82505
15°	0.88462	45°	0.85291	75°	0.81923
20°	0.87940	50°	0.84748	80°	0.81331
25°	0.87417	55°	0.84198		

The specific gravity of benzene from coal-tar oil was found to be 0.90122 and 0.90129 at 0°.

Pisati a. Paternò (*Gazz. chim. ital.* iv, 113) have made the following determinations of the specific gravity of benzene, obtained as a bye-product in the preparation of acetophenone by distilling a mixture of the calcium salts of acetic and benzoic acids, and purified by washing with water and with potash, and distillation over sodium:

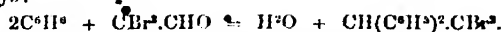
Temp.	Sp. gr.	Volume.
0°	0.899487	1.00000
15°	0.883573	1.01801
25°	0.872627	1.03078
50°	0.846170	1.06058
75°	0.818721	1.09865

The refractive index of benzene either from coal-tar oil or from benzoic acid, for the sodium line, is 1.4957 at 15.2° (Adriecenz).

Decompositions. 1. *By Heat.*—The statements of Berthelot (1st *Suppl.* 261) respecting the products obtained by passing benzene vapour through a red-hot tube, have been confirmed by G. Schultz (*Deut. Chem. Ges. Ber.* 1873, 415), so far as relates to the formation of diphenyl and of the bodies designated by Berthelot as chrysene, benzerythrene, and bitumene. Schultz also found paradiaphenyl-benzene, $C^{12}H^{14} = C^6H^4(C^6H^2)^2$, which he regards as identical with Berthelot's chrysene. He did not succeed in isolating from the products of the action of heat on benzene, a hydrocarbon identical with chrysene from coal-tar. Berthelot, on the other hand (*Bull. Soc. Chim.* [2], xxii, 437), refers to his own analysis for confirmation of the formula which he assigns to the chrysene obtained from benzene, viz. $C^{12}H^{14}$, which is that of triphenylene, $(C^6H^4)^3$, and points out that this hydrocarbon combines with picric acid, whereas Schultz's diphenylbenzene does not.

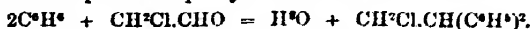
2. *By the action of Ozone.*—Houzeau a. Renard (*Compt. rend.* lxxvi, 572), by treating benzene with ozonised oxygen, have obtained—together with formic, acetic, and other acids—a gelatinous body, which dries up in a vacuum to a white amorphous solid. This substance, called ozobenzene, is very explosive, and detonates with great violence when struck or heated. It decomposes rapidly, either on exposure to the air, or in an atmosphere of carbon dioxide, or in a vacuum, being converted into a glutinous mass, and afterwards into a yellowish syrupy liquid containing a large quantity of acetic acid. Ozobenzene dissolves with decomposition in water, yielding formic, acetic, and a very soluble solid acid, which turns brown on addition of potash or soda, and reduces silver nitrate even in the cold. At the same time there is formed a fragrant substance which has no acid reaction.

3. *Reaction with Bromal.*—When 2 mols. benzene and 1 mol. bromal are mixed with about double the volume of strong sulphuric acid, diphenyl-tribromethane is produced, and gradually separates from the mass, the reaction being completed in two or three days:



Benzene and chloral in like manner yield diphenyl-trichlorethane (G. Goldschmidt, *Deut. Chem. Ges. Ber.* vi, 985).

4. *With Monochloraldehyde.*—When 2 mols. benzene and 1 mol. dichlorethyl oxide are agitated with strong sulphuric acid, the chloraldehyde produced by the action of the sulphuric acid on the dichlorethyl oxide (2nd *Suppl.* 481) reacts on the benzene in such a manner as to produce diphenyl-chlorethane:



The diphenyl-chlorethane thus formed is a pitchy substance which has not been obtained in a state fit for analysis, but evidence of its constitution is afforded by the fact of its being resolved by dry distillation into hydrochloric acid and a body, $CH^2 = C(C^6H^5)^2$, isomeric with stilbene (E. Hepp, *Deut. Chem. Ges. Ber.* vi, 1439). See DIPHENYL COMPOUNDS.

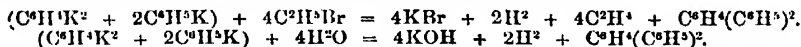
5. *With Formaldehyde.*—The product of this reaction is diphenyl-methane, $CH^2(C^6H^5)^2$ (2nd *Suppl.* 533).

Potassium-benzene (Abeljanz, *Deut. Chem. Ges., Ber.* v. 1027; ix. 10). When benzene and potassium are heated together in sealed tubes to 240°–250°, a certain quantity of benzene is absorbed, and a dry, blue-black, crystalline, kidney-shaped mass is formed, insoluble in excess of benzene. In contact with air it takes fire almost instantly, burning with explosive violence, and emitting an odour like that of diphenyl. It reacts violently with ethyl bromide, with water, and with iodine dissolved in benzene.

On bringing it in contact with ethyl-bromide under a layer of benzene, reaction begins at ordinary temperatures, attended with rapid evolution of ethene gas and formation of a brown-red mass, which after a while envelopes the benzene-potassium and prevents further action: the decomposition may, however, be completed by gentle heating in a water-bath. The brown-red mass consists of diphenyl-benzene, $C^6H_5(C^6H_5)^2$, agreeing in character with that which Riéso obtained by the action of sodium on mono- and di-bromobenzene (*2nd Suppl.* 945); m. p. 205. There is also formed a small quantity of an oily hydrocarbon having the composition $n.C^6H^2$.

In contact with water under a layer of benzene, benzene-potassium also yields diphenyl-benzene and the oil just mentioned, together with hydrogen and a small quantity of diphenyl.

These reactions show that benzene-potassium is not an addition- but a substitution-product. The formation of the several products may, indeed, be explained by supposing that the benzene-potassium is a mixture of the compounds C^6H_5K and $C^6H^2K^2$, in the proportion of 2 : 1; thus the principal reactions with ethyl bromide and with water may be represented by the following equations:—



In the second case, however, a small portion of the C^6H^2K escapes the principal reaction, and is converted into diphenyl:



As benzene-potassium is a substitution-product, hydrogen must be eliminated in its formation: this hydrogen, however, does not assume the gaseous form, but remains combined as potassium hydride, the presence of which may account for the explosive properties of the product.

Hydrogenation of Benzene and its Homologues (F. Wreden, *Liebig's Annalen*, cxxxvii. 153). According to Berthelot, these hydrocarbons, when heated to 270°–280° for ten to twenty-four hours with a saturated solution of hydriodic acid (sp. gr. 2.0) take up 8 atoms of hydrogen, and are converted into paraffins, either containing the same number of carbon-atoms as the original hydrocarbon (benzene into hexane, toluene into heptane, cymene into decane, &c.) or simpler ones formed therefrom by division (*1st Suppl.* 739). Wreden, on the other hand, finds that the aromatic hydrocarbons treated in this manner never take up more than 6 atoms of hydrogen, the final products being hydrocarbons of the general formula C^6H^{2n} , isomeric with the olefines. In their properties, however, these hydrocarbons resemble the paraffins rather than the olefines, being incapable of forming addition-products, offering great resistance to the action of oxidising agents, and yielding only to very powerful means of oxidation, in which case the molecule splits up and the chief products obtained are carbon dioxide and water.

The boiling points and specific gravities of these hexhydrated aromatic hydrocarbons are shown in the following table:—

	Boiling point.	Sp. gr. at 6°.	
C^6H^{12}	69°	0.76	
C^7H^{14}	97°	0.772	0.758 at 20°
C^8H^{16}	118°	0.781	0.765 at 20°
C^9H^{18}	135°–138°	(0.79)	} Water 6° = 1
$C^{10}H^{20}$	153°–158°	0.802	
			0.788 at 23°

The specific gravities exhibit a regular increase of 0.01 for a difference of CH^2 in the formula: that of hexhydromesitylene, C^9H^{18} , has not been directly observed, but is calculated according to this rate of increase. The boiling points of the last four members of the series exhibit an average difference of 20°.

The structure of these hydrocarbons may be represented by closed benzene-rings, in which all the carbon-atoms are singly linked, as in hexbromide and hexchloride of benzene (*1st Suppl.* 196).

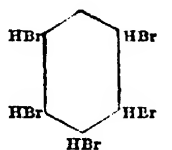
By fuming nitric acid or a mixture of nitric and sulphuric acids, these hydrocarbons are converted into nitro-derivatives of benzene and its homologues, e.g. C^6H^{12} into $C^6H^9(NO^2)_3$, C^6H^{16} into $C^6H^{13}(NO^2)_3$, C^6H^{18} into $C^6H^{15}(NO^2)_3$, &c., the reaction

consisting first in the removal of 6 atoms of hydrogen by oxidation, whereby the hydrocarbon C^6H^{12} is converted into an ordinary aromatic hydrocarbon, C^6H^6 , and secondly in the replacement of one or more atoms of hydrogen in this body by NO^2 .

The tendency of a hydrocarbon of the benzene series to take up an additional number of hydrogen-atoms appears to increase with the number of methyl-groups which it contains (perhaps generally with the number of its lateral chains): thus isoxylene, C^8H^{10} , treated with hydriodic acid and amorphous phosphorus, is completely converted into C^8H^{14} , whereas benzene and toluene similarly treated undergo no alteration.

By the regulated action of hydriodic acid (using weaker acid or stopping the action after a certain time) the hydrocarbon, C^6H^{12-6} , may be made to take up only 4 or 2 atoms of hydrogen; isoxylene, for example, may be converted into tetrahydro-isoxylene C^8H^{14} , &c. These incompletely hydrogenised bodies resemble the normal aromatic hydrocarbons C^6H^{12-6} in their behaviour with oxidising agents, being converted thereby into aromatic acids, $C^6H^{12-6}O^2$, containing equal numbers of carbon-atoms, tetrahydro-isoxylene, for example, into toluic acid, $C^8H^8O^2$.

Orientation in the Benzene series (Körner, *Gaze. chim. ital. iv.* 305-446). The determination of the relative positions of the substituted radicles in benzene-derivatives has hitherto been founded on the constitution of the three phthalic acids, which is itself deduced from that of naphthalene, mesitylene, and quinone (1st *Suppl.* 198, 203, 212; 2nd *Suppl.* 134). To this mode of treating the subject, however, exception may be taken on two grounds: 1. Because the reactions by which a di-derivative of benzene containing 6 atoms of carbon is converted into a phthalic acid, or other derivative containing a greater number of carbon-atoms, are not sufficiently simple and definite to afford a safe basis for determining the constitution of the 6-carbon di-derivatives.—2. Because the structural formulae of mesitylene, naphthalene, and quinone, which have hitherto formed the basis of the entire theory relating to the structure of the benzene-derivatives, are by no means established with certainty. Thus with regard to mesitylene, although it appears extremely probable, from its mode of formation, that it is a symmetrically constituted trimethylbenzene, yet its production from 3 mols. of acetone at a comparatively high temperature, accompanied as it is by the elimination of 3 mols. of water, justifies the doubt whether the reaction does not involve intramolecular change; and this doubt acquires further justification when the nature of the tribromobenzene from benzene hexbromide (i. 543) is considered. There is every reason to suppose that in the latter compound the hexagonal nucleus is preserved, and that the 6 atoms of hydrogen and of bromine are symmetrically disposed in the molecule; moreover, it is converted into tribromobenzene by a relatively very simple reaction. The most probable supposition with regard to this tribromobenzene would therefore appear to be that the three bromine-atoms are symmetrically disposed in the manner represented by figure I.; but Körner finds that it unquestionably has the constitution given by figure II.:



Benzene hexbromide.

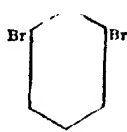


Fig. I.



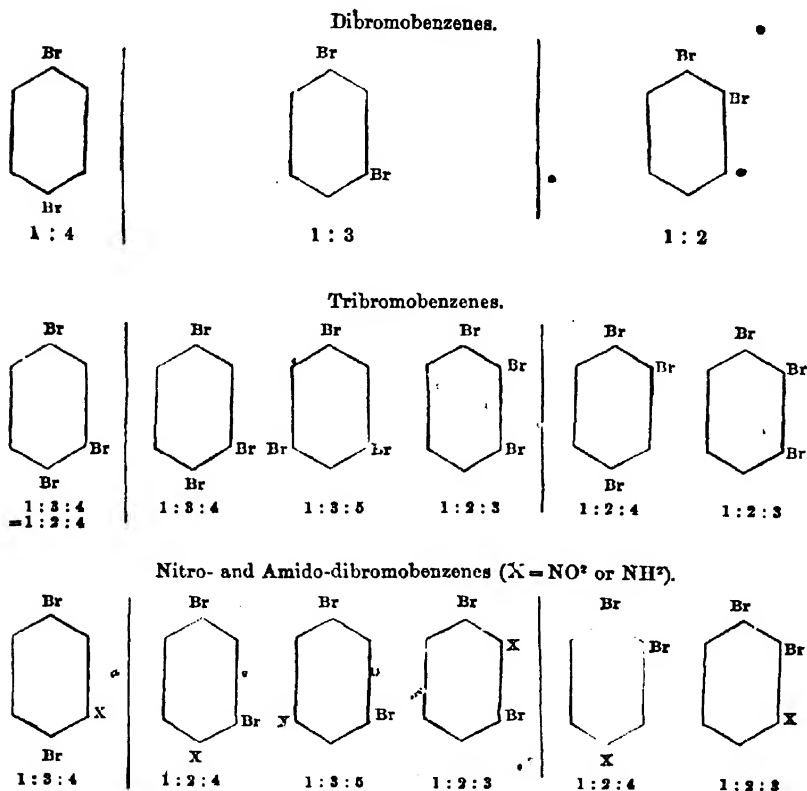
Fig. II.

Objection may also be urged against Graebe's conclusions as to the constitution of phthalic acid (1st *Suppl.* 212). His experiments prove only that naphthalene may be regarded as built up of two benzene-nuclei having 2 atoms of carbon in common; all speculation with regard to the relative positions of these two atoms of carbon is pure conjecture, and the conclusions as to the nature of phthalic acid are entirely dependent upon the kind of symbol employed to represent naphthalene: that is to say, whether the two carbon-atoms common to the two nuclei are assumed to be adjacent, as Graebe supposes, or non-adjacent. With regard to quinone, it is well known that Graebe's original conclusions as to the relative positions of the oxygen-atoms have recently been shown to be entirely unwarranted by facts (2nd *Suppl.* 924).

To avoid these sources of uncertainty, and to render the question of orientation independent—as far as possible—of hypotheses respecting the structure of any particular compounds, Körner has endeavoured to settle the constitution of the di- and tri-derivatives of benzene by a series of transformations in which only 6-carbon

compounds are concerned, selecting in all cases the most simple and direct methods, and especially avoiding the use of reagents which give rise to violent changes likely to alter the molecular structure of the bodies concerned.

The method in question consists mainly in studying the relations between the di-derivatives of benzene and the tri-derivatives which may be produced from them. Thus by converting the three isomeric dibromobenzenes into the three possible tribromobenzenes and the six possible nitrodibromobenzenes, and by preparing the three dibromobenzenes from the six possible dibromamidobenzenes or dibromanilines, the question of orientation may be completely resolved with regard to these several compounds, and therefore also with regard to all that are connected with them. This may be seen from the following table:—



This diagram shows: (1). That a para-derivative (1 : 4) can give rise to, and be derived from, only *one* tri-derivative, viz. the unsymmetrical modification, 1 : 2 : 4 or 1 : 3 : 4.

(2). That an ortho-derivative (1 : 2) can give rise to, and be produced from, *two* tri-derivatives, viz. the consecutive 1 : 2 : 3, and the unsymmetrical 1 : 2 : 4.

(3). That a meta-derivative (1 : 3) can give rise to, and be formed from, all the three tri-derivatives, 1 : 2 : 3, 1 : 3 : 4, and 1 : 3 : 5.

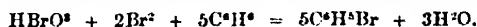
These conclusions, which are fully borne out by experiment, enable us to give definitions of the three classes of di-derivatives depending only on their relations to the tri-derivatives, and independent of all assumptions as to the relative positions of the substituted radicles; thus:

A di-derivative of benzene is para-, ortho-, or meta-, according as it can give rise to, and be formed from, one, two, or three tri-derivatives.

Bromobenzenes. MONOBROMOBENZENE, C_6H_5Br .—This compound may be advantageously prepared by the action of bromic acid on benzene.

When powdered potassium bromate (50 grams) and benzene (25–30 grams) are introduced into a flask half filled with sulphuric acid diluted with twice its weight of water, and the flask is agitated, the bromate gradually dissolves, and the mixture becomes warm. After some time, provided the temperature is not allowed to rise above 30° , the benzene is converted into a dense, colourless, oily body which, when dried over calcium chloride and rectified, distils for the most part at 155° , and has the composition and properties of monobromobenzene. A little dibromobenzene is almost always formed at the same time, especially if the temperature rises too high, or excess of bromate is employed. With only slightly diluted sulphuric acid the products are entirely different.

In this reaction the oxygen of the bromate plays the part of one-half of the bromine in the process usually employed. To render available the oxygen present in the bromate in excess of that so acting, it is only necessary to add bromine and a corresponding quantity of benzene, in about the proportion shown by the equation :



Practically it is better to use rather less bromine and more bromate than are thus indicated. The yield is 70–80 per cent. of the theoretical amount (Krafft, *Deut. Chem. Ges. Ber.* viii. 1044).

Properties.—Monobromobenzene (prepared by the action of bromine on benzene) boils at 154.86° – 155.52° . Its refractive index for the sodium line is 1.5595 at 15° . Its sp. gr. at different temperatures is as follows:—

Temperature	0°	11.46°	20.96°	77.70°
Sp. gr.	1.51768	1.50236	1.48077	1.41163

(Adrienz, *Deut. Chem. Ges. Ber.* vi. 441).

DIBROMOBENZENE, $C_6H_4Br_2$.—Three modifications of this compound are known, two liquid at ordinary temperatures, the third solid and melting at 89° (*2nd Suppl.* 139). Of the two liquid modification, one, obtained by Riese, together with the solid, by the action of bromine on benzene, was observed by him to solidify at -27° in crystals which melted at -1° ; the other, which Meyer and Stüber obtained by treating ordinary dibromaniline (from acetyl chloride) with nitrous acid and alcohol, does not solidify even at -28° .

Recent experiments by Meyer (*Deut. Chem. Ges. Ber.* vii. 1560) have shown, however, that the crystals which separate from Riese's liquid dibromobenzene really consist of the crystalline isomeride (m. p. 81°), and that by cooling strongly and carefully removing the crystals which form, and repeating these operations six or eight times, a product is ultimately obtained which no longer solidifies even at -28° .

So far, then, the two liquid dibromobenzenes obtained respectively from benzene and from dibromaniline, might be supposed to be identical; but that they are really distinct modifications, is shown by the crystallographic examination of their mononitro-derivatives, the nitrodibromobenzene (m. p. 60° – 61°) prepared from Meyer and Stüber's dibromobenzene crystallising in small, four-sided, almost rectangular forms of the triclinic system, whereas the nitrodibromobenzene (m. p. 58°), obtained from Riese's dibromobenzene, crystallises in monoclinic forms (pp. 177, 178).

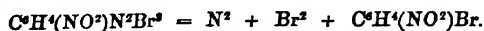
The orientation of the bromine-atoms in these three isomeric bodies was not, however, very satisfactorily determined by the experiments above mentioned. The dibromobenzene obtained from dibromaniline was recognised as the meta-modification, because when treated with chlorocarbonic ether and sodium amalgam, it yielded bromobenzoic and isophthalic acids (Wurster, *Lieber's Annalen*, clxxiii. 145); but the crystalline modification was regarded by Meyer as para-, by v. Richter as ortho-dibromobenzene (*2nd Suppl.* 140).

The question has, however, been completely determined by the researches of Körner (*Gazz. chim. ital.* iv. 331), who has solved it, as already described (p. 162), by examining the relations between the three dibromobenzenes on the one hand, and the three tribromobenzenes, mononitrodibromobenzenes, and dibromanilines on the other, the result being that the solid dibromobenzene (m. p. 89°) is the para-modification, the liquid modification obtained from ordinary dibromaniline the meta-, and the liquid modification formed, together with the solid, by direct bromination of benzene, the ortho-modification.

Preparation.—The three dibromobenzenes may be obtained in pure and definite form, either by the action of phosphorus pentabromide on the corresponding oxyphenols (hydroquinone, &c.), or by the diam-reaction from the corresponding nitraui-

lines (iv. 430-438). The latter method is preferred, because the former, though more direct, involves the expenditure of a large quantity of costly material.

The nitranilines are first converted into the corresponding diazonitrobenzenes, $C^6H^4(NO^2)N^2$, by treating the solutions of their nitrates with nitrous acid; the diazo-compounds are converted by the action of bromine-water into perbromides, $C^6H^4NO^2.HBr^2$; and these latter, decomposed by boiling with alcohol, yield the corresponding nitrobenzenes:



In this manner may be obtained: paranitrobromobenzene, melting at 125.5° ; meta-, at 54.6° ; ortho-, at 43.1° .

These compounds are reduced by tin and hydrochloric acid to bromanilines, which are distilled off with excess of potash, then converted into nitrates; and the nitrates, finely pulverised and suspended in nitric acid, are treated with excess of nitrous acid; the resulting diazobromobenzenes are converted into perbromides by treatment with the calculated quantity of bromine dissolved in bromide of potassium; and lastly, the perbromides finely pulverised, are converted into the corresponding dibromobenzenes, in the case of the para-derivative by boiling with absolute alcohol, in the cases of the meta- and ortho-derivatives (which do not yield pure products when thus treated), by distillation with sodium carbonate. The mixture of the perbromide with sodium carbonate requires special precautions, on account of the rapidity of the action which ensues. The best mode of proceeding is to half-fill with the pulverised carbonate a retort previously fitted to a very long condenser, then as quickly as possible add the perbromide, cover it up with a layer of carbonate, and immediately close the retort with the stopper. The retort is then shaken, so as to mix the materials, whereupon a violent action ensues, causing half the product to distil over at once, without the aid of heat. When this reaction is over, the retort must be gradually heated, and finally, to a rather high temperature.

The products thus obtained are purified by washing with water from free bromine and small quantities of bromophenols, then distilled with aqueous vapour, dried with phosphoric anhydride, and rectified (Körner, *Gazzetta*, iv. 333).

According to Wurster a. Grubenmann (*Deut. Chem. Ges. Ber.* vii. 416), the nitrobenzene required for the preparation of metadibromobenzene, is most readily obtained by the action of ethyl nitrite on bromaniline (m. p. 104.5°). Acetanilide is brominated by means of bromine-water, and the dry bromo-derivative nitrated by dissolving it in a cooled mixture of nitric and sulphuric acid, and pouring the product into water. The nitrobromacetanilide is then decomposed by heating it with a solution of sodium hydrate, and the bromonitraniline treated with nitrous ether. After removing a portion of the alcohol by distillation, the product is precipitated by water, and the resulting bromonitrobenzene purified by pressure and repeated crystallisation from alcohol, and subsequent distillation in a current of steam.

V. v. Richter (*ibid.* viii. 1425) observes that when bromine-water is added to the nitric acid solution of diazobenzene at ordinary temperatures, the perbromide is precipitated as an oil which solidifies after a while, and yields a product consisting chiefly of dibromobenzene; whereas if the bromine-water be added to the diazo-compound previously cooled with ice, the perbromide separates in yellow flocks which yield, by decomposition with alcohol, scarcely anything but tribromobenzene. It appears, therefore, that in the latter case, the diazobenzene perbromide undergoes further bromination by the action of bromine-water, which does not take place when the perbromide separates in the liquid form.

Paradibromobenzene (1 : 4).—This modification, prepared either from paranitraniline in the manner just described, or by the action of phosphorus pentabromide on parabromophenol, is identical with that which Couper obtained by the action of bromine on benzene or monobromobenzene. The simplest way of preparing it is to heat benzene for several days with excess of bromine, till the mixture solidifies on cooling. The product may be decolorised by means of potash, then recrystallised several times from boiling alcohol, and afterwards distilled. All the secondary products formed in the reaction remain in the mother-liquors, provided care has been taken to prevent the formation of large crystals.

Paradibromobenzene forms perfectly white crystals melting at 89.3° and boiling at 218.6° , under a pressure of 757.7 mm. It sublimes, though very slowly, at ordinary temperatures, forming splendid, strongly refracting crystals. It has a peculiar odour, recalling that of *Mentha aquatica*. It dissolves with difficulty in cold alcohol, in considerably larger quantity in hot alcohol and ether, and separates, especially by slow evaporation of a mixture of alcohol and ether, in well-defined crystals. Nitric acid of sp. gr. 1.54 dissolves it slowly, at ordinary temperatures if it is in the state of

powder, more quickly at a gentle heat, transforming it in either into mono-nitro-*para*-dibromobenzene, melting at 85.4° (Körner).

Metadibromobenzene, (1 : 3), is an oil of peculiar odour, quite different from that of the *para*-compound. It remains liquid at -20°, boils at 219.4°, under a pressure of 754.80 mm.; has a sp. gr. of 1.355 at 18.6° (that of water at 4° being taken for unity). It is quickly attacked by nitric acid of sp. gr. 1.4, provided the temperature of the air is not too low; with weaker acid, a slight rise of temperature is necessary to start the action. The resulting solution gives with water a crystalline precipitate consisting of two mononitrodibromobenzenes, the more abundant melting at 61.6°, the other at 82°.

Identical with this metadibromobenzene is: (1) that which Meyer & Stüber obtained by the action of ethyl nitrite on ordinary dibromaniline, which, in its turn, may be prepared either from dibromacetanilide, or by reduction of the nitrometadibromobenzene, $C_6H_3Br_2(NO_2)H.H$, which melts at 61.6°. (2) That which results from the reduction of symmetrical nitrodibromobenzene (1 : 3 : 6), melting at 104.5°, and treatment of the resulting dibromaniline with ethyl nitrite. (3) The nitrometadibromobenzene (1 : 2 : 3), melting at 82.6° (which is itself formed from metadibromobenzene), should also yield the same modification, but this conversion has not yet been actually effected.

Orthodibromobenzene (1 : 2).—This modification should be identical with Riese's liquid dibromobenzene, obtained, together with the *para*-compound, by the action of bromine on benzene. According to Körner, however, it cannot be obtained pure by this process, and in fact, Riese's statements as to its boiling point and other physical properties differ considerably from those of Körner. According to Riese, its boiling point is between 212° and 215° (corr.), which is below that of the solid *para*-modification (219°), whereas according to Körner it boils at 223°-224°. It crystallises at -6° and melts at -1°. Its sp. gr. is greater than that of metadibromobenzene, being 2.003 at 0°, 1.997 at 17.6°, and 1.858 at 99°. Its refracting power is also greater than that of the *meta*-compound, and its odour is totally different from those of the other two dibromobenzenes. With the strongest nitric acid it yields a nitro-product, which solidifies but slowly and partially. The chief product of the reaction, after repeated crystallisation from alcohol, melts, in accordance with Riese's statement, at 57.8° (Körner).

The following table exhibits a comparative view of the properties of the three dibromobenzenes as determined by Körner (compare Meyer's table, 2nd Suppl. 130):

Dibromobenzenes	Melting point	Boiling point	Mononitro-derivatives
<i>Para</i> (1 : 4): produced from paranitraniline, identical with that of Couper. <i>Meta</i> (1 : 3): from ordinary dinitrobenzene prepared from metanitraniline; identical with that which Meyer & Stüber obtained from ordinary dibromaniline, and with that which is derived from nitrodibromobenzene melting at 104.5°.	89°	218.4° under 747 mm. at 21.3°	Yields a single mononitro-derivative melting at 85.4°.
<i>Ortho</i> (1 : 2): from orthonitrobromobenzene and orthonitraniline.	liquid at -20°	219.4° under 754.8 mm. at 19°	Yields with nitric acid two mononitro-derivatives, one melting at 61.6°, the other at 82.6°. There is also a third nitro-metadibromobenzene melting at 104.5°, but not obtained by direct methods.
	about -1°	223.8° under 751.64 mm. at 18.2°	Gives with nitric acid two mononitro-derivatives, the chief product melting at 57.8°.

BROMIODOBENZENES, C_6H_4BrI (Körner, *Gazz. chim. ital.* iv. 339).—The three modifications were prepared by the action of hydriodic acid on the diazo-compounds obtained from the corresponding monobromanilines; the *para*- and *ortho*-modifications also from the respective iodonilines, through the medium of the perbromides of the corresponding diazo-compounds.

Parabromiodobenzene, $C_6H_3Br.I.H_2$, crystallises in tables and prisms of peculiar odour, distantly resembling that of *para*dibromobenzene. It is very slightly soluble in cold alcohol, moderately soluble in hot alcohol, more soluble in ether.

From a mixture of 1 mol. alcohol and 2 mol. ether, it separates in better-defined crystals, perfectly colourless and transparent, not coloured by diffused daylight, but becoming coloured after prolonged exposure to the direct solar rays. It melts at 91.9° and boils at 251.5° – 251.6° under a pressure of 754.44 mm. at 21.8° . Nitric acid acts on it with violence, even in presence of a very large quantity of acetic acid, the greater part of the iodine being liberated and replaced by NO^2 , so that the chief product is para-nitrobromobenzene.

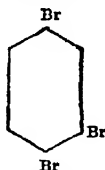
Metabromiodobenzene, $\text{C}^6\text{H}_4\text{Br.I.H}^3$, is a liquid, colourless when freshly prepared, but acquiring a rose-colour in course of time, and having an odour somewhat like that of iodobenzene. Boils quite constantly at 252° under a pressure of 754.44 mm. at 21.8° . It dissolves easily in tepid nitric acid of sp. gr. 1.54, without separation of iodine, yielding a mixture of nitro-compounds, the most abundant of which is nitro-metabromiodobenzene, melting at 126.8° .

Orthobromiodobenzene, $\text{C}^6\text{H}_4\text{Br.I.H}^4$, is a colourless liquid smelling like impure metadiodobenzene, and becoming coloured on exposure to the sun's rays. Boils at 257.4° under 754.44 mm. at 21.8° . Nitric acid of sp. gr. 1.54, if free from lower oxides of nitrogen, dissolves it easily without separation of iodine, yielding a mononitro-derivative.

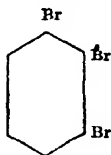
These three bromiodobenzenes exhibit differences of boiling point almost exactly the same as those of the corresponding dibromobenzenes; the para- and meta-bromiodobenzenes boil at nearly the same temperature, the meta- a little higher (0.6°) than the para-, and the ortho-derivative about 6° higher than the meta-:

	Dibromobenzenes.	Bromiodobenzenes.
Para- . . .	218.4 $^{\circ}$	251.5 $^{\circ}$
Meta- . . .	219.4 $^{\circ}$	252.0 $^{\circ}$
Ortho- . . .	223.8 $^{\circ}$	257.4 $^{\circ}$

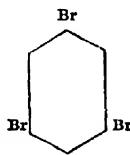
TRIBROMOBENZENES, $\text{C}^6\text{H}_3\text{Br}^3$ (Körner, *Gazzetta*, iv. 401).—Of the three possible modifications of the tribromobenzenes, viz.:



1 : 3 : 4 = 1 : 2 : 4
Unsymmetrical.



1 : 2 : 3
Consecutive.

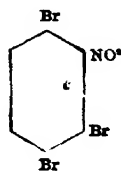
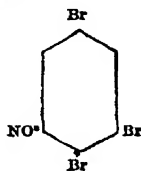
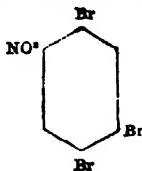


1 : 3 : 5
Symmetrical.

one was prepared many years ago by Mitscherlich (i. 543) from benzene hexbromide, and subsequently by A. Mayer, by the action of phosphorus pentabromide on ordinary dibromophenol (1st *Suppl.* 263), also by Griess from ordinary dibrom-aniline by substitution of bromine for the ammonia residue NH^2 (*Ann. Ch. Pharm.* cxxvii. 22.); a second has recently been obtained by Körner from dibromoparanitraniline; and the third is described by Stüber (*Deut. Chem. Ges. Ber.* iv. 961), as resulting from the action of ethyl nitrite on ordinary tribromaniline.

By reference to the diagram on p. 162, it will be seen that of these three tribromobenzenes, the first (1 : 3 : 4 or 1 : 2 : 4) may be derived from either of the three dibromobenzenes; the second (1 : 2 : 3) from two, viz. 1 : 3 or 1 : 2; the third (1 : 3 : 5) from only one, viz. 1 : 3.

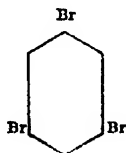
The constitution of a tribromobenzene is therefore known when the number of modifications of dibromobenzene from which it may be formed is determined. Another mode of determining the constitution of these bodies is furnished by the study of their nitro-derivatives. It is clear, indeed, that the tribromobenzene which is capable of furnishing three mononitro-derivatives, or can be produced from either of these three, must have the constitution 1 : 3 : 4. This modification is, in fact, contained in the three following nitrobromobenzenes:—



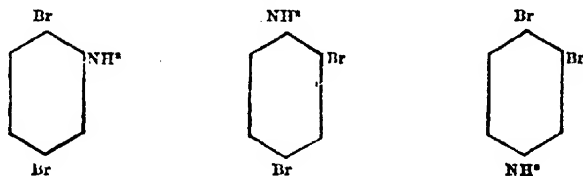
The tribromobenzene 1 : 2 : 3 gives rise to, and can be produced from, only two mononitro-derivatives, viz. :—



and with regard to the third tribromobenzene, 1 : 3 : 5, in which the three bromine-atoms are arranged symmetrically, it is absolutely indifferent in which of the three remaining places the group NO^2 is introduced, the same nitrotribromobenzene resulting in each case, viz. 1 : 3 : 4 : 5 or—



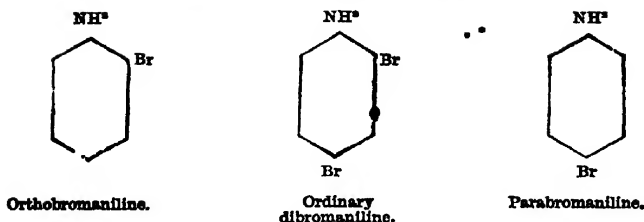
A third method of determining the structure of a tribromobenzene is based upon the following considerations. Of the six possible nitrodibromobenzenes, three, and consequently the three dibromanilines produced by their reduction, belong to the series of derivatives having their replaced hydrogen-atoms in the positions 1 : 2 : 4 (p. 162).



On the other hand, two of the six nitrotribromobenzenes (p. 162), have their three bromine-atoms in the positions 1, 2, 3. Hence it follows that the tribromobenzene formed from either of these last nitro-derivatives by inverse replacement of the group NO^2 , must also be the consecutive modification 1 : 2 : 3; in like manner, the three dibromanilines above figured must lead, by substitution of Br for NH^2 , to one and the same tribromobenzene 1 : 2 : 4.

Unsymmetrical Tribromobenzene,* $\text{C}^6\text{H}_3\text{Br}_3$.—This is the modification which Mitscherlich obtained by the action of alkalis on the hexbromide of benzene, $\text{C}^6\text{H}_6\text{Br}_6$, produced by the action of bromine on benzene in sunshine (i. 643). It has also been obtained by the action of phosphorus pentabromide on ordinary dibromophenol (A. Mayer, *Ann. Ch. Pharm.* cxxxvii. 224); and by the diazo-reaction from ordinary dibromaniline (Griess, *Phil. Trans.* cliv. 667). This last mode of formation determines its constitution. For ordinary dibromaniline may be formed either from ortho- or from para-bromaniline, by converting either of these bases into bromacetanilide by the action of a large excess of acetyl chloride, treating the resulting cry-talline mass under water with bromine (1 mol.), whereby it is converted into dibromacetanilide, saponifying this product, and distilling in a current of steam. The bromaniline thus obtained must have one of its bromine-atoms in the ortho- and the other in the para-position with regard to the NH^2 , and consequently its two bromine-atoms in the *meta*-position with regard to each other—that is to say, it must have the constitution 1 : 2 : 4 (NH^2 in 1), or 1 : 3 : 4 (Br in 1).

* The unsymmetrical tri-derivatives of benzene, having two of their substituted radicles in the position 1 : 4, may also be conveniently distinguished by the prefix *para*; the symmetrical, in which all three of these radicles are to one another in the position 1 : 3, by the prefix *meta*; and the consecutive, by the prefix *ortho*.



Hence also the tribromobenzene formed from this dibromaniline, by substitution of Br for NH_2 , must have the constitution 1 : 3 : 4, or 1 : 2 : 4, its three bromine-atoms being respectively in the positions 1 : 2, 1 : 3, and 1 : 4, with regard to each other.

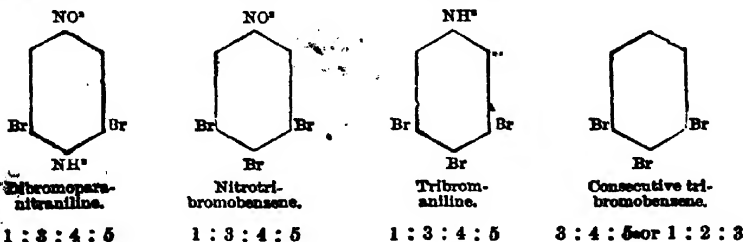
To prepare this compound from dibromaniline, the nitrate of that base suspended in somewhat dilute nitric acid is subjected to the action of a strong current of nitrous acid, till it is completely dissolved, and the resulting solution of diazo-bromobenzene, largely diluted with water, is mixed with a solution of bromine (in calculated quantity and in the form of potassium bromide) in hydrobromic acid; and the yellow perbromide thus obtained, after being washed with water, drained on a porous tile, and dried, is distilled with a large excess of sodium carbonate. By washing the product with water, distilling at first in a current of steam, and then alone, and drying with phosphoric anhydride, the tribromobenzene is obtained as a liquid which boils at 275° - 276° , and solidifies on cooling to a white crystalline mass composed of small needles.

This tribromobenzene melts at 44° , and boils at 275° , sublimes even at ordinary temperatures; dissolves with difficulty in alcohol even when warmed. Nitric acid of sp. gr. 1.54 dissolves it, even at ordinary temperatures, forming two mononitro-derivatives, the most abundant of which melts at 93.5° .

Since ordinary dibromaniline may be formed by reduction of nitrometadibromobenzene, which is a derivative of metadibromobenzene, the above-described preparation of Mitscherlich's tribromobenzene from ordinary dibromaniline, may be regarded as a transformation of metadibromobenzene effected by the (indirect) introduction of a third atom of bromine; and the tribromobenzene in question may be designated as bromo-metadibromobenzene.

The same tribromobenzene may also be obtained by precisely similar transformations, from ortho-dibromobenzene, and from para-dibromobenzene, and may accordingly be regarded either as bromo-ortho- or as bromo-para-dibromobenzene; and its derivation from either of the three modifications of dibromobenzene affords an additional proof that it belongs to the series of benzene-derivatives represented by the formula 1 : 3 : 4. The same conclusion may also be drawn respecting the three nitrodibromobenzenes employed in its preparation, and respecting the corresponding dibromanilines and nitro-bromanilines.

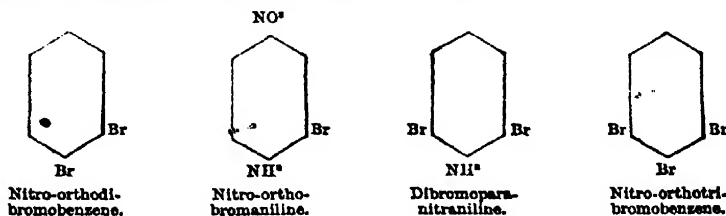
Consecutive Tribromobenzene, $\text{C}_6\text{Br}_3\text{Br}.\text{H}^2$.—This modification is obtained by a series of transformations from dibromoparanitraniline, $\text{C}_6\text{Br}_2\text{NH}_2.\text{Br}.\text{H}.\text{NO}^2.\text{H}$, melting at 202.5° . This base, treated by the diazotization, yields a nitrotribromobenzene, $\text{C}_6\text{Br}_2\text{Br}.\text{Br}.\text{H}.\text{NO}^2.\text{H}$, which, by reduction of the group NO^2 , and replacement of the resulting group NH_2 by hydrogen (by the action of ethyl nitrite) yields consecutive tribromobenzene. This series of transformations is more clearly represented by the following formulae:—



The tribromobenzene distilled with steam and purified by crystallisation from alcohol forms large rhombic tablets, perfectly transparent and colourless, having a

strong lustre, but partly losing their transparency when exposed to the air. It melts at 87.4° , sublimes easily, dissolves in nitric acid of sp. gr. 1.49, and separates unaltered on addition of water. By prolonged heating with nitric acid of sp. gr. 1.54 it is converted into a nitro-compound.

The structure of this tribromobenzene may also be demonstrated in the following manner. The dibromoparanitraniline from which it is derived has its two bromine-atoms relatively in the position 1 : 3. Now, as this same dibromoparanitraniline may also be prepared from nitro-orthobromaniline (derived from nitro-orthodibromobenzene, $C^6H_3Br_2NO_2$), and reconvertible into the latter, it follows that at least one of its two bromine-atoms must be in the ortho-position with regard to the NH^2 ; and since the bromine introduced in place of the residue NH^2 necessarily takes the place of this residue, it follows that this third atom of bromine must likewise occupy the ortho-position with regard to at least one of the bromine-atoms already existing in the dibromoparanitraniline. The nitro-tribromobenzene thus produced will therefore have the structure 1 : 3 : 4 : 5 :—



Moreover, since the reduction of the group NO_2 to NH^2 , and the replacement of the latter by hydrogen cannot alter the positions of the three bromine-atoms, it follows that the resulting tribromobenzene will have its three bromine-atoms in the position 3 : 4 : 5 or 1 : 2 : 3.

Symmetrical Tribromobenzene, $C^6H_3Br_3$.—This, which is the only remaining formula possible for a tribromobenzene, must evidently belong to the modification which Stüber obtained by the action of ethyl nitrite on ordinary tribromaniline, prepared by treating aniline hydrochloride with bromine (*Deut. Chem. Ges. Ber.* iv. 96). The reaction begins in the cold and is completed by warming. The cooled solution subsequently deposits the tribromobenzene in the form of long

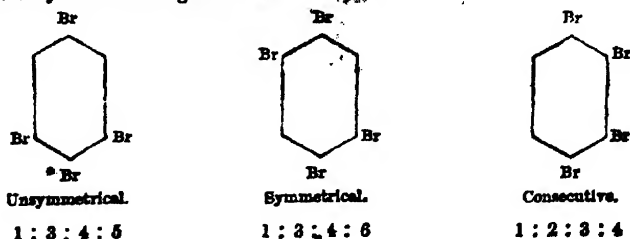
above 278° (Körner).

The same tribromobenzene may be prepared from the dibromaniline (m. p. 56.6°) obtained by reduction of nitrometadibrombenzene (p. 177). The nitrate of this dibromaniline is converted by nitrous acid into the corresponding diazo-compound,

of tri-derivatives 1 : 3 : 5.

According to Körner, dilute nitric acid does not act on symmetric tribromobenzene, and nitric acid of sp. gr. 1.54 converts it at once into a dinitro-compound. According to C. L. Jackson, on the other hand (*Deut. Chem. Ges. Ber.* viii. 1172), this tribromobenzene is converted by fuming nitric acid into a mononitro-compound, and by a mixture of fuming nitric and strong sulphuric acid into a dinitro-compound (p. 181).

TETRABROMOBENZENES, $C^6H_2Br_4$.—The three possible modifications are represented by the following formulæ:—



Unsymmetrical Tetrabromobenzene is produced: (1). By the action of PBr^3 on ordinary tribromophenol melting at 95° (1st Suppl. 263), which has the constitution $\text{C}^6\text{OH.Br.H.Br.H.Br}$ (see table, 2nd Suppl. 929), and will therefore yield, by substitution of Br for OH, a tetrabromobenzene represented by the first of the above figures (1 : 2 : 4 : 6, or 1 : 3 : 4 : 5).—(2). By substitution of Br for NH^2 in ordinary tribromaniline, $\text{C}^6\text{NH}^2\text{H.Br.Br.Br.H}$. This may be effected by passing nitrous acid vapour into glacial acetic acid in which tribromaniline is suspended till the latter is dissolved, and treating the resulting diazo-compound with concentrated hydrobromic acid, whereby the liquid is converted into a magma of crystals of diazo-tribromobenzene bromide; and this when boiled with more glacial acetic acid, as long as nitrogen continues to be given off, yields crystals of tetrabromobenzene, which may be purified by crystallisation. The conversion is, however, most simply effected by mixing strong hydrobromic acid with tribromaniline and glacial acetic acid, and passing nitrous gas into the warm mixture till nitrogen is no longer evolved.

Unsymmetrical tetrabromobenzene crystallises in long needles, very sparingly soluble in alcohol and melting at 98.5° . Heated with nitric acid of sp. gr. 1.50, it yields pure mononitrotetrabromobenzene, $\text{C}^6\text{Br.NO}^2\text{Br.Br.Br.H}$, which crystallises from alcohol in prisms melting at 96° ; with acid of sp. gr. 1.52 it yields a mixture of mono- and dinitro-compounds; and with acid of sp. gr. 1.54, pure dinitrotetrabromobenzene, $\text{C}^6\text{Br.NO}^2\text{Br.Br.Br.NO}^2$, which crystallises from benzene in large prisms melting at $227^\circ\text{--}228^\circ$, and is deposited from boiling alcohol as a crystalline powder (V. v. Richter, *Deut. Chem. Ges. Ber.* viii. 1426; see also Wurster a. Nölting, *ibid.* vii. 1564).

β . Another modification of tetrabromobenzene, melting at 160° , according to Riche a. Bérard, at $137^\circ\text{--}140^\circ$ according to Kekulé (iv. 414), is obtained by heating benzene, paradibromobenzene, or (1 : 2 : 4) tribromobenzene with bromine. Now either of these compounds might yield, by further bromination, either the consecutive or the symmetrical modification of tetrabromobenzene, or both together: hence it is impossible to determine the constitution of this modification from its mode of formation; and no reaction by which the question might be settled appears to have been yet discovered. On the other hand, the wide difference between the boiling points, given by Kekulé and by Roche a. Bérard, seems to indicate that the methods of preparation above given may actually give rise to two different modifications of tetrabromobenzene.

PENTABROMOBENZENE, C^6HBr^5 , produced, together with unsymmetrical tetrabromobenzene, by heating nitro- or dinitrobenzene with bromine to 200° , forms silky needles melting above 240° (1st Suppl. 263).

HEXABROMOBENZENE, C^6Br^6 (E. Gessner, *Deut. Chem. Ges. Ber.* ix. 1505).—This compound is obtained by the action of iodised bromine on benzene, toluene, or azobenzene.

1. Iodised bromine is dropped into cooled benzene, whereupon a brisk evolution of hydrobromic acid takes place; and the resulting crystallised mass is heated by small portions in sealed tubes, first to $80^\circ\text{--}100^\circ$ till but little hydrogen bromide escapes on opening the tubes, then gradually to higher temperatures, and finally, for twenty to thirty hours, at $250^\circ\text{--}400^\circ$. The product is then digested with soda-ley to remove free bromine and iodine, recrystallised from boiling toluene, washed with alcohol, and sublimed between watch-glasses.

2. Toluene, treated with iodised bromine in the manner above described, is resolved into perbromobenzene, perbromomethane, and hydrobromic acid:



The product obtained at 250° consists of quadratic laminæ, which at a higher temperature are converted into needles, and on treating this last product with soda-ley, to remove iodine and excess of bromine, and then distilling it with water, a small quantity of crystalline substance passes over consisting of perbromomethane, and a residue is left consisting of hexbromobenzene. As the quantity of perbromomethane obtained was but small, it is probable that the greater portion of this compound formed in the first instance had been subsequently converted into hexbromobenzene: $6\text{CBr}^4 = \text{C}^6\text{Br}^6 + 9\text{Br}^2$.

γ . Azobenzene, mixed with bromine, becomes hot without at first giving off any gas; after a while, however, especially on addition of a little iodine, a violent evolution of hydrogen bromide takes place. On heating the mixture to 100° and then leaving it to cool, the product solidifies in a mass of slender needles, and by raising the temperature to 300° , afterwards to 350° , and maintaining this latter temperature

for forty-five hours, nearly the whole is converted into hexabromobenzene. The reaction is :



The crude product is purified by crystallisation from toluene and chloroform.

Hexbromobenzene is very much like hexchlorobenzene, but its melting point is much higher, viz., above 310° ; on the other hand, it burns much more readily than the chlorinated derivative; but if the air be excluded, it sustains a moderate red heat without alteration. It dissolves with moderate facility in boiling benzene and toluene, more readily in boiling aniline and oil of turpentine, with difficulty in boiling ligroin, glacial acetic acid, and chloroform, and crystallises from all these solutions in beautiful white needles; the finest crystals, having the form of long, shining needles, are obtained from a saturated solution in hot chloroform. In alcohol and ether it is almost insoluble. It sublimes with moderate facility in plumose tufts of needles sometimes an inch long.

Chlorobenzenes. MONOCHLOROBENZENE, C^6H^5Cl , is formed, together with benzene sulphonylchloride and thionyl chloride, by distilling potassium benzene-sulphonate with an equal weight of phosphorus pentachloride. The quantity of monochlorobenzene obtained, increases with the proportion of phosphorus pentachloride used, and when the benzene sulphonylchloride is heated with the pentachloride for some hours in sealed tubes to 200° – 210° , it is completely decomposed, according to the equation :

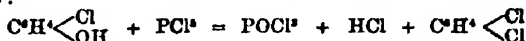


(Barbaglia a. Kekulé, *Deut. Chem. Ges. Ber.* v. 875).

The boiling points, refractive indices, and specific gravities of monochlorobenzene, prepared from benzene and from phenol, have been determined by Adrieensz (*Dent. Chem. Ges. Ber.* vi. 441), with the following results:—

		from Benzene		from Phenol
Boiling point (at 760 mm.)		131°5'—131°9'		132°4"—132°58'
Index of refraction for sodium lime		1·528		1·5255
Specific gravity at		0° 1·12855	at	0° 1·12818
" " " " " "		9-79° 1·11807	"	12-93° 1·11421
" " " " " "		22-43° 1·10467	"	20-96° 1·10577
" " " " " "		77-27° 1·04428	"	73-15° 1·04299

DICHLOROBENZENE, $C_6H_4Cl_2$. The several modifications of this compound are formed from the corresponding monochlorophenols by the action of phosphorus pentachloride:



Ortho-dichlorobenzene, thus prepared, is a liquid which does not solidify at -14° , boils at 179° (thermometer in the vapour), and has a density of 1.3278 at 0° . With fuming nitric acid it yields two nitro-derivatives, $(C^6H^3(NO_2)Cl)_2$, one liquid, the other crystallising in needles which melt at 43° . It unites at 210° with fuming sulphuric acid, forming a sulpho-acid, whose barium salt, $(C^6H^3ClSO_3^2Ba + 2H^2O)$, crystallises in rhombic plates. It is also formed, together with the para-modification, by direct chlorination of benzene (Beilstein & Kurbatow, *Deut. Chem. Ges. Ber.* vii. 1398, 1759).

Metadichlorobenzene, $\text{C}_6\text{H}_4\text{Cl}_2$, may be prepared: (1.) By transforming the nitrate of metanitraniline obtained from ordinary dinitrobenzene, into the corresponding diazo-compound, and adding to the solution properly diluted with water, an excess of platonic chloride, whereby a light orange-yellow precipitate is formed; and this, when dried and distilled with sodium carbonate, yields metanitrochlorobenzene, which may be freed by washing with aqueous potash from a small quantity of a phenolic product formed at the same time, then distilled with steam, and finally purified by two crystallisations from alcohol. By reduction it yields an oily metachloraniline, which does not solidify when cooled by snow. On treating the nitrate of this base with a rapid current of nitrous acid, and precipitating the resulting solution of diazo-chlorobenzene with platonic chloride, after dilution with water, a precipitate of diazo-chlorobenzene platinumchloride is obtained, which, when washed with water, dried, and distilled with sodium carbonate, yields metadichlorobenzene:



The distillate is washed with potash, distilled with vapour of water, dried with phosphoric anhydride, and finally subjected to fractional distillation.

2. Ordinary dichloraniline, prepared by the action of chlorine on acetanilide, and distillation of the resulting dichloroacetanilide with potash (iv. 440), is converted by the action of ethyl nitrite into meta-dichlorobenzene, identical with that prepared by the first method (Körner, *Gazz. chim. Ital.* iv. 341).

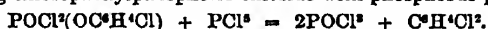
Metadichlorobenzene is a colourless oil, having an odour similar to that of meta-dibromobenzene, but somewhat more powerful. It boils at 172.1° under a pressure of 742.40 mm. at 15° (Körner), at 171° – 172° (Beilstein a. Kurbatow), at 170° – 171° (Witt), and does not solidify in a mixture of ice and salt. Nitric acid of sp. gr. 1.52 attacks it violently, forming a mixture of nitro-compounds, the chief of which is a dinitro-metadichlorobenzene. With weaker nitric acid a mononitro-dichlorobenzene is obtained, which melts at 32.2° (p. 185), (Körner).

Paradichlorobenzene, $C^6Cl_2H_4$ (Barbaglia a. Kekulé, *Deut. Chem. Ges. Ber.* v. 876; Kekulé, *ibid.* vi. 943; Beilstein a. Kurbatow, *ibid.* vii. 1396, 1769; Körner, *Gazz. chim. ital.* iv. 342).

This modification is formed: (1.) By direct chlorination of benzene in presence of a small quantity of iodine, the product thus obtained being purified by treatment with potash, distillation with steam, drying with phosphoric anhydride and fractional distillation. As thus prepared, however, it always retains a small quantity of iodine (Körner).

According to Aronheim (*Deut. Chem. Ges. Ber.* viii. 1400), the chlorination of the benzene is greatly facilitated by the presence of about 1 per cent. of *molybdenum pentachloride*, much more indeed than by iodine. The chlorine is then rapidly absorbed, and, after the removal of hydrochloric acid and molybdenum pentachloride by washing with water, the whole of the benzene is found to be converted into crystalline dichlorobenzene, mixed with only a small quantity of oily liquid consisting of *ortho*- and *tri*-chlorobenzenes. 2. By the action of phosphorus pentachloride on *parachlorophenol* (Beilstein a. Kurbatow).

3. By heating chlorophenylphosphoric chloride with phosphorus pentachloride:



Hence it is formed in the action of PCl_5 on chlorophenylphosphoric acid, the first product of which is chlorophenylphosphoric chloride, and is also found in considerable quantity among the products obtained by heating the potassium salt of *phenolpara-sulphonic acid* with phosphorus pentachloride, the direct product of which is also chlorophenylphosphoric chloride.* On rectifying the product of this reaction, nothing but thionyl chloride and phosphorus oxychloride passes over at 60° – 120° , while the high-boiling portion consists of an oil from which chlorophenylphosphoric chloride may be obtained by fractional distillation, the intermediate portions yielding by decomposition with water a large quantity of dichlorobenzene, together with phosphoric, hydrochloric, and monochlorophenolphosphoric acid, which dissolve in the water (Kekulé).

Paradichlorobenzene obtained by either of these processes is solid at ordinary temperatures, melts at 53° and boils at 172° (Beilstein a. Kurbatow), at 173.2° under a pressure of 757.6 mm. (Körner).

In the direct chlorination of benzene, a small quantity of a liquid dichlorobenzene is obtained, consisting of a mixture of the *ortho*- and *para*-modifications. On treating this liquid with moderately strong fuming sulphuric acid, the *ortho*-modification is readily dissolved, whilst the *para*-dichlorobenzene, which unites but slowly with the acid and only after prolonged heating, crystallises out on mixing the solution with water. The liquid freed from excess of sulphuric acid by baryta, and heated in an oil-bath, gives off *ortho*-dichlorobenzene, which, after washing with water and distillation, boils constantly at 179° , and is converted by nitric acid into dichloronitrobenzene melting at 43° (Beilstein a. Kurbatow).

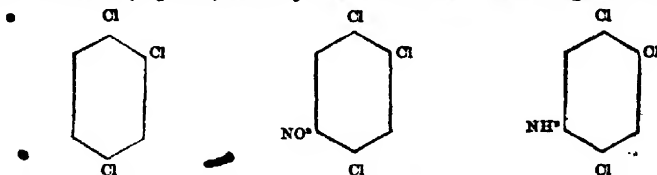
PARACHLOROBROMOBENZENE, C^6ClH_3Br .—Prepared.—1. By decomposing the platinocloride of diazobromobenzene, obtained from octahedral bromaniline. 2. By decomposing the perbromide of diazochlorobenzene, prepared from octahedral chloraniline. 3. By boiling pure monochlorobenzene with excess of bromine till the mixture crystallises on cooling. The products thus obtained are absolutely identical, melting at 67.4° , and boiling at 196.3° , under a pressure of 756.12 mm. at 19.6° . In other respects this chlorobromobenzene exactly resembles *paradibromobenzene* (Körner, *Gazzetta*, iv. 342).

ORTHOIODOBENZENE.—The *para*-modification, C^6ClH_3I , prepared by the *diano*-reaction from *para*-chloraniline, crystallises in large colourless prisms and tablets, having a peculiar odour, and much more soluble in alcohol than *parabromiodobenzene*. After drying with phosphoric anhydride, it boils constantly at 227.6° , under a pressure of 761.26 mm. at 27° . When treated with nitric acid it yields only a small quantity of nitro-*parachloriodobenzene*, other compounds being formed at the same time, with elimination of iodine (Körner, *ibid.* 343). According to Beilstein a. Kurbatow, it melts at 56.57° , and boils at 226° – 227° .

Orthochloriodobenzene, $C^6Cl_2H_3I$, prepared in like manner from pure *ortho*-

chloraniline (freed from the para-modification by means of hydrochloric acid, which dissolves chiefly the latter), is a colourless oil smelling like iodobenzene, and boiling above 233° (Körner), at 229° – 230° , and having a sp. gr. of 1.928 at 24.5° (Beilstein a. Kurbatow). Nitric acid converts it into nitro-iodobenzene, without separation of iodine (Körner).

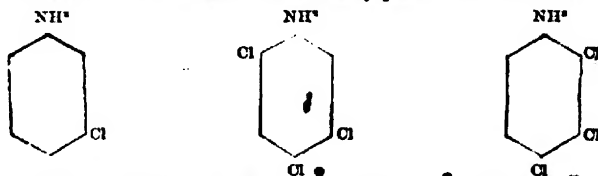
TRICHLOROBENZENES, $C^6H^2Cl^3$ (Beilstein a. Kurbatow, *Deut. Chem. Ges. Ber.* x. 270).—1. *Unsymmetrical* (1 : 2 : 4).—This modification was first prepared in the pure state by Jungfleisch, who obtained it by direct chlorination of benzene (2nd Suppl. 141). It may also be prepared by the action of PCl^3 on dichlorophenol, $C^6H^2Cl^2.OH.Cl.H.Cl.H^2$ (m.p. 42° – 43°), and from either of the dichloranilines, 1 : 2 : 4 and 1 : 3 : 4 (NH^2 in 1), by replacing the NH^2 with chlorine. It melts at 16° and boils at 213° (thermometer in the vapour). By solution in strong nitric acid, it is converted into nitro-trichlorobenzene (m.p. 58°), which yields a trichloraniline melting at 95° – 96° :—



The *sulpho-acid*, $C^6H^2Cl^3.SO^3H$, obtained by heating this trichlorobenzene with fuming sulphuric acid, forms barium, calcium, and lead salts, which crystallise in needles containing $2H^2O$, e.g. $(C^6H^2Cl^3SO^3)^2Ba + 2H^2O$.

2. *Symmetrical* (1 : 3 : 5).—Formed by treating ordinary trichloraniline 1 : 2 : 4 : 6 (NH^2 in 1) with ethyl nitrite (Körner; Beilstein a. Kurbatow). It melts at 63.5° and boils at 208.5° (bar. at 763.8 mm.; thermometer in the vapour). Dissolves sparingly in alcohol and in acetic acid of 50 per cent., easily in ether, light petroleum, carbon disulphide and benzene. By nitration it is converted into $C^6.NO^2.Cl.H.Cl.H.Cl$, melting at 68° .

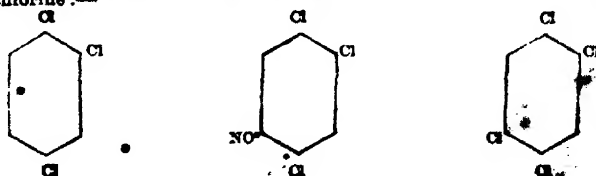
3. *Consecutive* (1 : 2 : 3).—Metachloracetanilide (1 mol.) treated with chlorine (2 mols.), yields the acetyl-derivatives of two isomeric trichloranilines easily separable by their different solubility in 50 per cent. acetic acid. The less soluble consists of the acetyl-derivative of the trichloraniline with unsymmetrically distributed chlorine-atoms, the more soluble of that with consecutively placed chlorine atoms :



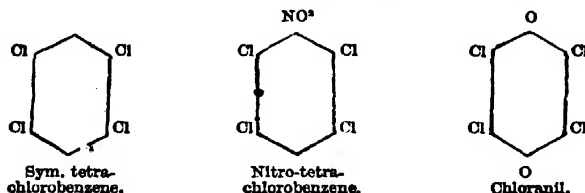
The acetyl-derivatives boiled with caustic soda yield the corresponding trichloranilines, the second of which is converted by ethyl nitrite into consecutive trichlorobenzene.

This trichlorobenzene melts at 53° – 54° and boils at 218° – 219° . From alcohol, in which it is somewhat sparingly soluble, it crystallises in large tables. Its nitro-derivative, $C^6.NO^2.Cl.Cl.Cl.H^2$, forms needles having a silky lustre and melting at 55° – 56° , convertible by reduction into trichloraniline with consecutive chlorine-atoms (Beilstein a. Kurbatow).

TETRACHLOROBENZENES, $C^6H^2Cl^4$.—1. *Symmetrical* (1 : 2 : 4 : 5).—This, which is the ordinary modification, melts, according to Jungfleisch, at 139° , and boils at 240° . Beilstein a. Kurbatow obtain it from unsymmetrical trichlorobenzene (1 : 2 : 4), by converting this compound into nitro-trichlorobenzene, 1 : 2 : 4 : 5 (NO^2 in 5), and the corresponding trichloraniline (m.p. 95° – 96°), and replacing the NH^2 , by chlorine :—



Symmetrical tetrachlorobenzene melts at 137° – 138° , and boils at 243° – 246° (thermometer in the vapour). By solution in strong nitric acid it is converted into nitro-tetrachlorobenzene, $C^4HCl^4(NO^2)$, melting at 98° – 99° , yielding at the same time a certain quantity of tetrachloroquinone (chloranil), separable from the nitro-compound by its insolubility in light petroleum. The formation of chloranil is very characteristic of this modification of tetrachlorobenzene (neither of the others yielding it), and affords a further corroboration of the para-position of the oxygen-atoms in chloranil:



2. *Unsymmetrical* (1 : 3 : 4 : 5).—Obtained, but not in the pure state, by Jungfleisch, and by Otto and Ladenburg, the melting points found by these chemists varying from 27° to 35° , the boiling points from 245° to 253° . Beilstein a. Kurbatow obtain it from ordinary trichloraniline, $C^6H^3Cl^3.H.Cl$ (1 : 2 : 4 : 6), by substitution of Cl for NH^2 . From alcohol, in which it dissolves but slightly at ordinary temperatures, it crystallises in needles. It melts at 50° – 51° , and boils at 246° . By solution in nitric acid (sp. gr. 1.62), it is converted into $C^6Cl.NO^2.Cl.Cl.Cl.H$, melting at 21° – 22° .

3. *Consecutive* (1 : 2 : 3 : 4).—Produced from trichloraniline, $C^6H^3Cl^3.H.Cl$, by substitution of Cl for NH^2 . It crystallises in needles, melts at 45° – 46° , boils at 254° . By nitration it yields nitro-tetrachlorobenzene, $C^6Cl.Cl.Cl.Cl.Cl.NO^2.H$, melting at 64.5° , and reducible by tin and hydrochloric acid to tetrachloraniline, which crystallises from light petroleum in broad needles melting at 118° (Beilstein a. Kurbatow).

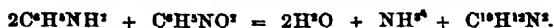
The discovery of this consecutive modification completes the series of the chlorinated derivatives of benzene.

Nitrobenzenes. *Mononitrobenzene*, $C^6H^5NO^2$, oxidised with manganese dioxide and sulphuric acid, yields as chief product an acid which has the composition of nitrobenzoic acid, and crystallises in large plates melting at 234° (Hassenpflug, *Deut. Chem. Ges. Ber.* viii. 1188).

Action of Ammonium Sulphite.—Hilkenkamp (*Ann. Ch. Pharm.* xcv. 36), by heating 1 mol. nitrobenzene with 3 mols. ammonium sulphite, the mixture being kept alkaline by addition of solid ammonium carbonate, obtained a product consisting mainly of ammonium sulphanilate, $C^6H^4.NH.SO^2NH^4$. Carius, by the same process, obtained ammonium disulphanilate, $C^6H^4(NH.SO^2NH^4)_2$, (v. 479). J. A. Roorda Smit (*Deut. Chem. Ges. Ber.* viii. 1442), proceeding in the same manner, and continuing the reaction for four days, has obtained a product which corroborates Hilkenkamp's result.

Action of Chlorine.—Chlorine alone does not act on nitrobenzene, but in presence of iodine, or better, of antimonious chloride, it is rapidly absorbed, with formation of metachloronitrobenzene, $C^6Cl.H.NO^2.H$ (Laubenheimer, *see* p. 182).

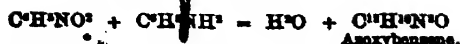
Action of Aniline.—A mixture of aniline (2 mols.) and nitrobenzene (1 mol.), saturated with hydrochloric acid gas and heated to 230° in sealed tubes from which the air has been expelled, is converted into ammonium chloride, water, and a blue-black solid, the solution of which in alcohol and acetic acid deposits, on addition of potash, a base having the composition of triphenylene-diamine:



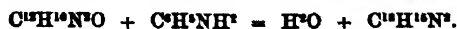
The same base is formed, together with water but no ammonia, when a mixture of nitrobenzene and diphenylamine in equivalent proportions, is saturated with hydrochloric acid and heated to 230° in sealed tubes:



When nitrobenzene and aniline hydrochloride are heated to 160° – 170° in an open vessel, a diphenyl-diamine is formed by elimination of water, probably in two stages, thus:—



Asoxybenzene.



Asodiphenyldiamine.

The second of these equations has been verified by direct experiment. At high temperatures in sealed tubes, ammonia is eliminated and triphenylene-diamine is formed as above (v. Dechens a. Wichelhaus, *Deut. Chem. Ges. Ber.* viii. 1609).

DINITROBENZENE, $\text{C}^6\text{H}^4(\text{NO}^2)^2$ (Rinne a. Zincke, *Deut. Chem. Ges. Ber.* vii. 869; Körner, *Gazz. chim. ital.* iv. 354).—The dinitrobenzene obtained in the ordinary way by treating benzene or mononitrobenzene with fuming nitric acid, is a mixture of three isomerides, the most abundant being the ordinary dinitrobenzene, which crystallises from alcohol in needles or laminae, melting, according to most authorities, at 86° . This modification, formerly regarded as *para*-, has subsequently been shown to consist of *meta*-dinitrobenzene (2nd Suppl. 924).

To prepare pure *metadinitrobenzene*, Körner proceeds as follows: Pure crystallisable mononitrobenzene is gradually added, without cooling, to a mixture of equal volumes of nitric acid (sp. gr. 1.54) and fuming sulphuric acid in quantity sufficient to dissolve it completely. The whole is then heated from twelve to fourteen hours in covered flasks, till a sample of the oily product which separates on the surface solidifies on cooling. The mixture is then poured in a thin jet, and with constant agitation, into a very large quantity of water; the product, which separates in a fine state of division, is collected after a while in large funnels without filters; and the greater part of the remaining nitric acid is removed by washing with water under a tap. The crude dinitrobenzene is then pulverised and thoroughly washed in a displacement apparatus, ultimately with distilled water. The product is then dried and dissolved in a large quantity of boiling alcohol, and the solution cooled by immersing the vessel in cold water. The crystalline mass which separates is again introduced into a displacement apparatus, and washed with tepid water till the washings are no longer coloured on addition of alcohol containing ammonia. After one or two crystallisations from strong alcohol, perfectly pure *metadinitrobenzene* is obtained in thin, colourless, opaque or semi-transparent, flexible needles, melting at 89° . In this respect—and this alone—it differs from the somewhat impure dinitrobenzene, prepared in the ordinary way, the melting point of which is usually given as 86° .—100 pts. alcohol of 99.3 per cent. dissolve 5.2 parts of *metadinitrobenzene* at 24.6° ; the same alcohol at the boiling heat dissolves it in all proportions.

The *metaphenylene-diamine* prepared from this pure dinitrobenzene does not yield by oxidation a trace of quinone. Hofmann, on the other hand, found that the *diphenylene-diamine* prepared from ordinary dinitrobenzene gave on oxidation a small quantity of quinone, which continually diminished as the dinitrobenzene was further purified by recrystallisation, and ultimately disappeared altogether. Its formation was in all probability due to the presence of a small quantity of the *para*-modification (Körner).

When an alcoholic solution of *metadinitrobenzene* is treated with sodium-amalgam the temperature rises quickly, and the liquid, according to its degree of concentration, becomes blue, red, or green, and finally black, these changes of colour being probably due to the formation and subsequent decomposition of nitrosophenylin, the compound which Church and Perkin obtained by the action of zinc on dinitrobenzene (iv. 115). On pouring the solution into water, a black insoluble precipitate separates, and the supernatant alkaline liquid remains of a blackish-brown colour. When hydrochloric acid is added to the alkaline filtrate, a black precipitate is thrown down, which possesses acid properties, is insoluble in the ordinary solvents, and gives by analysis numbers agreeing with the empirical formula, $\text{C}^{10}\text{H}^6\text{N}^2\text{O}^2$. This substance is not attacked by tin and hydrochloric acid; nitric acid converts it into a yellow amorphous body; and sodium-amalgam acts on its alkaline solution, with evolution of ammonia, but without formation of definite products (Michler, *Liebig's Annalen*, clxxv. 150).

Alcoholic solutions of caustic soda and potash produce a lively reaction with dinitrobenzene, and black amorphous substances are formed, which are partly soluble in alkalis (Michler).

***Para*-dinitrobenzene, $\text{C}^6\text{H}_4\text{NO}^2\text{H.H.NO}^2\text{H}^2$** .—When the alcoholic mother-liquors obtained in the purification of crude dinitrobenzene are left at rest for some time, crystalline masses are deposited which, when recrystallised, afford

moderately soluble in ether, benzene, and chloroform, slightly soluble in cold alcohol, almost insoluble in water. By reduction with ammonium sulphide, it yields a substance

iline melting at 146° , and with tin and hydrochloric acid a phenylene-diamine melting at 140° . These results show that the dinitrobenzene just described is a *para*-derivative (Rinne a. Zincke).


Orthodinitrobenzene, $C_6H_4(NO_2)_2$.—The crystalline crusts deposited as above mentioned, from the alcoholic mother-liquors of crude dinitrobenzene, contain also a third modification, which may be separated from the two others by repeated crystallisation from dilute acetic acid. It crystallises from hot water in long colourless opaque needles, and from acetic acid in striated plates or serrated needles, melting at 117° – 118° . When more strongly heated it sublimes in fern-like plates. In alcohol, benzene, and chloroform, it is less soluble than the meta-compound, and crystallises from these solutions in well-defined plates. By hydrogen sulphide in presence of alcohol, it is reduced to orthonitraniline, melting at 70° – 71° (not at 66° as formerly stated), and by tin and hydrochloric acid to orthophenylenediamine, melting at 99° . * This third dinitrobenzene is, therefore, the *ortho*-modification (Rinne a. Zincke, *ibid.* 1372; see further Körner, *loc. cit.*)

Nitrobromobenzene, $C_6H_4(NO_2)Br$. The statements respecting the three modifications of this compound in the 2nd Suppl. (pp. 142, 143), require considerable alteration, according to the results of more recent investigations. The *ortho*- and *para*-modifications (not the *meta*-) are formed by the action of fuming nitric acid on monobromobenzene. The *para*-modification, which crystallises out first, melts at 126° , and is reduced by ammonium sulphide or ferrous acetate to parabromaniline, melting at 64.5° . The *ortho*-modification, which crystallises from the mother-liquors, forms long needles melting at 37° (Hübner a. Alsberg), at 41° (Meyer). By reduction with tin and hydrochloric acid, it yields orthobromaniline, melting at 31° and boiling at 22.9° (2nd Suppl. 944). *Metanitrobromobenzene* is the modification which Griess obtained by heating the perbromide of β -azonitrophenylammonium with sodium carbonate (iv. 416). It melts at 56° , and is reduced by ammonium sulphide to meta-bromaniline.

Dinitrobromobenzenes, $C_6H_3Br(NO_2)_2$. a. (Br : NO_2 : NO_2 = 1 : 2 : 4).—Prepared by the action of a mixture of strong nitric and sulphuric acids on monobromobenzene. Large crystals melting at 79.3 (Fittig's Grundriss d. org. Chemie, 10te Auflage, p. 343).

b. (Br : NO_2 : NO_2 = 1 : 3 : 4). Obtained in like manner from (1 : 3) nitrobromobenzene. Yellow prisms or tablets melting at 59.4° (Fittig).

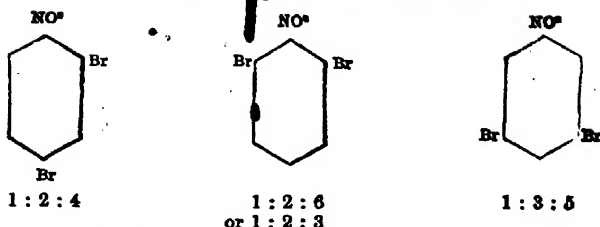
Nitrodibromobenzenes, $C_6H_2Br_2NO_2$. Of the six possible modifications of this compound (p. 162), one melting at 85° , and produced by the action of nitric acid on paradibromobenzene, has long been known (iv. 416), and more recently two others, produced in like manner from the other two dibromobenzenes, have been obtained by Riese and by Meyer a. Stüber. The properties of these bodies were, however, but very imperfectly known till their examination was undertaken by Körner (*Gazz. chim. ital.* iv. 360).

Nitroparadibromobenzene, .—This is the first of the three modifi-

cations above mentioned. It melts at 85.4° , and crystallises from a mixture of alcohol and ether in large yellow-green transparent tablets, notwithstanding of exact measurement on account of the curvature of some of their faces. Some of the angles, however, agree with those of the corresponding chlorine-derivative, so that these two compounds appear to be isomorphous. A mixture of fuming nitric and sulphuric acids converts it into two isomeric dinitrodibromobenzenes. With reducing agents it yields the dibromaniline of Meyer a. Wurster (Br : NH_2 : Br = 1 : 2 : 4), which when its ammonia residue NH_2 is replaced by bromine, yields unsymmetrical tribromobenzene (p. 168).

Nitrometadibromobenzene.—Cf this compound there are three modifications represented by the formulae :

* In Walker a. Zincke's memoir 'Ein drittes Nitranilin' (*Deutsch. Chem. Ges. Ber.* v. 114), the nitrobenzene melting at 146° is regarded as the *ortho*-, and that which melts at 66° as the *para*-modification (2nd Suppl. 944). Subsequent observations, however, have shown that these designations must be reversed.



a. (1 : 2 : 4). This modification, analogous to ordinary dibromaniline, is formed by treating metadibromobenzene with nitric acid, either strong or dilute. With acid of sp. gr. 1.54 and an external temperature not below 20° , the action is rapid and attended with rise of temperature; with weaker acid heat must be applied; in either case the yield of nitrodibromobenzene is but small, the quantity increasing, however, with the strength of the acid. The product is precipitated and washed with water, then crystallised from boiling alcohol. It forms needle-shaped crystals which, when left for a few hours in the mother-liquor, are converted into a group of small yellow-greenish prisms; and by pulverising these crystals, washing them repeatedly with alcohol, and recrystallising from boiling alcohol, the compound is finally obtained pure in tablets having the colour of native sulphur and melting at 61.6° .

According to measurements by Groth and Bodewig (*Deut. Chem. Ges. Ber.* vii. 1562), these crystals are small four-sided, nearly right-angled, triclinic prisms exhibiting the combination $\infty P \infty \cdot \infty P \infty \cdot OP$, with ∞P and $\infty P'$ subordinate, and rarely P' :—

a (brach.) b (macr.) c (vertical)
 Axial ratio: 0.8870 : 1 : 1.6960

Angles of the three axial planes:

$A = 66^\circ 32'$; $B = 97^\circ 12'$; $C = 89.1^\circ$.

Angles of the axes ($b : c$; $c : a$; $a : b$):

$\alpha = 66^\circ 28'$; $\beta = 97^\circ 25'$; $\gamma = 92^\circ 4'$.

No cleavage. The directions of polarisation on all the vertical faces are oblique to the axis c .

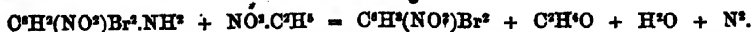
The crystals melt at 61.6° ; are slightly soluble in cold, easily in hot alcohol, the saturated solution depositing the compound in the form of an oil which solidifies on cooling. It volatilises easily with aqueous vapour, and sublimes unaltered if gradually heated. A mixture of fuming nitric and sulphuric acids converts it readily into dinitrometadibromobenzene melting at 118.4° . By reduction with tin and hydrochloric acid, it is converted into ordinary dibromaniline, $\text{O}^2\text{BaHBr}(\text{NH}^2)\text{H.H.}$

β . The second modification ($\text{Br} : \text{NO}^2 : \text{Br} = 1 : 2 : 3$) remains in the last alcoholic mother-liquors of the preceding, and is ultimately deposited as an oil, from which large colourless prisms gradually separate. These, when mechanically collected and recrystallised, yield colourless prisms or laminae, melting at 82.6° , sublimable and volatilising with aqueous vapour. By sudden cooling from a hot saturated solution the compound is obtained in white opaque needles having a silky lustre. Heated in sealed tubes with ammonia to a temperature above 180° , it is converted into a nitro-metaphenylene-diamine very soluble in alcohol, crystallising therefrom in red-brown needles, and convertible by nitrous ether into nitrobenzene. Heated for five or six hours with a mixture of fuming nitric and sulphuric acids, it yields a dinitrometadibromobenzene totally different from that above mentioned.

γ . *Symmetric Nitrometadibromobenzene*, $\text{NO}^2 : \text{Br} : \text{Br} = 1 : 3 : 5$.—This compound is formed by the action of nitrous ether on either of the two nitrodibromanilines:



The base must be treated in a flask connected with a long condensing tube, with a saturated solution of nitrous acid in absolute alcohol, kept in excess during the whole of the process. The action commences without external heating; the mixture becomes hot, gives off nitrogen and vapour of aldehyde; and the nitrobromaniline dissolves:

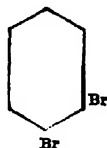


Towards the end of the process it is best to apply a gentle heat and add a little more nitrous ether. The solution on cooling deposits the nitrodibromobenzene in slightly coloured needles, an additional quantity of which may be obtained by evaporation of the mother-liquors. The product, washed with a little alcohol, distilled with vapour of water, and crystallised once or twice from boiling alcohol, forms thin, transparent, nearly colourless, flexible, elastic lamellar crystals, 2 or 3 mm. broad, and extending from one side of the containing vessel to the other. It is sublimable, and melts at 104.5° . From ether it crystallises in large prisms or tablets, which are likewise transparent and colourless, have angles of 45° and 90° , and cannot be bent without breaking.

This nitrodibromobenzene is very stable, not being acted on by the most concentrated alcoholic ammonia, even when heated therewith in sealed tubes to 215° for several weeks. Towards 220° , however, decomposition sets in, the mixture turns brown, small red-brown needles are formed, and after heating for a few hours the tubes burst. A mixture of fuming nitric and sulphuric acid acts on the nitrodibromobenzene as slowly as it does on metanitrobromobenzene (1 : 3), the introduction of another NO^2 into the molecule requiring in both cases the use of a large excess of the most concentrated acids at the temperature of the water-bath.

By reducing the same nitrodibromobenzene with tin and hydrochloric acid, and distilling with excess of potash in a current of steam, the corresponding dibromaniline, $\text{C}^6(\text{NH}^2)\text{HBrHBrH}$, is obtained, which crystallises in very white needles, melts at 56.5° , and exhibits rather strong basic properties.

Nitro-orthodibromobenzenes.—Of the two possible ortho-modifications:



1 : 3 : 4



1 : 2 : 3

only the first is at present known. It is produced by the action of nitric acid on orthodibromobenzene. Nitric acid of sp. gr. 1.54 instantly dissolves this compound, the action being more violent in proportion as the dibromobenzene is more impure. Weaker acid acts less rapidly, requiring the aid of heat if the dibromobenzene is quite pure. On pouring the product into water, an oily liquid separates, which slowly concretes into a pasty mass; and from this, the principal product may be extracted by dissolving it in hot absolute alcohol, and recrystallising the crystals which separate therefrom, once from glacial acetic acid, and two or three times from absolute alcohol.

Nitro-orthodibromobenzene, when pure, forms fan-shaped groups of long yellowish-green needles, or when crystallised from dilute solutions by spontaneous evaporation, large transparent prisms; when not quite pure, it crystallises in very slender white needles. According to Groth and Bodewig (*Deut. Chem. Ges. Ber.* vii. 1563), the crystals are monoclinic tables, $0\text{P} \cdot \infty\text{P}$ with $\infty\text{R}\infty$ quite subordinate. As no pyramids or domes are present, the ratio of the vertical axis to the other two could not be determined. Cleavage perfect parallel to $\infty\text{P}\infty$, distinct parallel to $\infty\text{R}\infty$. The plane of the optic axes is parallel to the plane of symmetry. These axes are inclined at an angle of about 60° .

The compound melts at 58.6° , and sublimes at a very gentle heat. By a mixture of nitric and sulphuric acids, it is easily transformed into a di-nitro-orthodibromobenzene. By the action of reducing agents it is converted into dibromaniline melting at 80.4° , distinguished from ordinary dibromaniline by the energy of its basic properties, and convertible by the diazo-reaction into unsymmetric tribromobenzene, $\text{C}^6\text{BrBrHBrHH}$.

The same nitro-dibromobenzene heated to 180°–190° for several days in a sealed tube with very concentrated alcoholic ammonia yields an unsymmetrical (1:3:4) bromonitraniline, $C^6H_3Br_2NH^2.H.Br.NH^2.H^2$, which crystallises in very slender needles of a fine canary-yellow colour, melting at 104.5°.

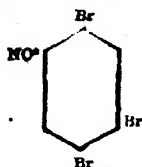
Dinitro-orthodibromobenzene, $C^6H_3Br_2H.NO^2$.—A body of this composition is obtained by the action of a mixture of nitric and sulphuric acid on ortho-dibromobenzene. When purified by repeated crystallisation from glacial acetic acid, it forms large white shining prismatic crystals melting at 168°. Heated to 100° in sealed tubes with ammonia, it is slowly attacked, yielding a deep-red liquid which is readily acted on by amyl nitrite, with formation of a mono-bromodinitrobenzene, which melts at 87°, and is not affected by ammonia.

The acetic acid from which this dinitrodibromobenzene was crystallised contained two other bodies: 1. A second dinitrodibromobenzene crystallising in small white needles, melting at 120°, and acted upon in alcoholic solution by ammonia at 100°, with formation of a pale yellow bromodinitraniline melting at 167°–170°. 2. A red oil which, when heated to 100° with alcoholic ammonia, yielded a body crystallising in orange-red scales and melting at 100°. The positions of the two NO^2 groups in these dinitrodibromobenzenes are at present undetermined (P. T. Austen, *Deut. Chem. Ges. Ber.* viii. 1132).

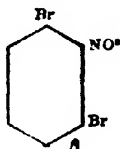
Nitro-tribromobenzenes, $C^6H^2Br_3.NO^2$. Six modifications of this compound are possible, three derived from unsymmetrical (para-), two from consecutive (ortho-) and one from symmetrical (meta-) tribromobenzene. Of these one was obtained in 1864 by A. Mayer (*Ann. Ch. Pharm.* cxxvii. 226), by the action of hot strong nitric acid on unsymmetrical tribromobenzene, and four others have lately been prepared by Körner (*Gazzetta*, iv. 412).

1. **Nitroparatribromobenzene**.—The action of nitric acid on unsymmetrical tribromobenzene gives rise to two mononitro-derivatives, the chief product being identical with that obtained by Mayer (m.p. 93.5°), while the less abundant, which separates from the mother-liquors of the former, does not melt at 187°. A third modification, melting at 119.5°, is formed by substitution of Br for NH^2 in dibromorthonitraniline.

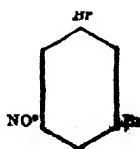
The constitution of the first and third of these derivatives has been determined by Körner experimentally, whence also that of the second becomes known:



m.p. 93.5°.



solid at 187°.



m.p. 119.5°.

Nitroparatribromobenzene, $C^6H_2Br_3.H.Br.Br.Br.NO^2$, melting at 93.5°. Unsymmetrical monobenzene dissolves readily in a large excess of nitric acid of sp. gr. 1.54; with the acid prolonged heating is required, and a small quantity of bromopicroin is formed at the same time. The solution obtained in either case gives with water a yellow precipitate of the nitrotribromobenzene, which, when washed, dried, and repeatedly crystallised from a large quantity of alcohol, forms long needles of a light yellow-green colour. From ether containing a little alcohol, it separates by spontaneous evaporation in large sulphur-yellow, transparent crystals (apparently monoclinic pyramids). It may be sublimed if cautiously heated, volatilises quickly with vapour of water, dissolves sparingly in cold alcohol, in larger proportion in hot alcohol and in ether; it is soluble also in glacial acetic acid, especially when warmed. By heating with alcoholic ammonia it is converted into the corresponding nitro-bromoparatribromobenzene, $C^6H^2Br_3.NH^2.H.Br.NH^2.H.NO^2$.

Nitroparatribromobenzene, $C^6H_2Br_3.H.Br.Br.Br.NO^2.H$, melting at 119.5°.—This modification is prepared by the diazo-reaction from the dibromorthonitraniline $C^6H_2Br_3.H.Br.NH^2.NO^2.H$, obtained by the action of bromine on nitroparabromaniline, $C^6H_3Br_2.H.Br.NH^2.NO^2.H$. The dibromonitraniline suspended in nitric acid of sp. gr. 1.38, is exposed to a rapid current of nitrous acid gas; the resulting solution, if necessary, is treated with a solution of bromine and potassium bromide in hydrobromic acid; the orange-yellow precipitate, after washing with water and draining, is decomposed by boiling alcohol; and the crystalline residuum left on evaporating the alcoholic solution is repeatedly distilled with vapour of water till it becomes

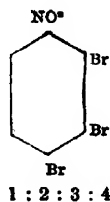
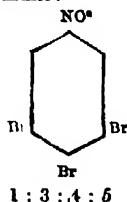
colourless. The substance thus obtained is a mixture of two compounds, which may be separated by crystallisation from acetic acid, the chief product separating therefrom in long white needles, while the mother-liquors yield a small quantity of another substance not yet analysed, which crystallises in yellow tablets. The needles consist of nitroparatribromobenzene melting at 119.5° ; they are grouped in tufts and have a strong silky lustre. The compound, heated to 140° with alcoholic ammonia, is reconverted into the dibromonitraniline from which it was prepared.

Nitroparatribromobenzene, $C^6H_3Br_3NO^2$, not fusible at 187° .—This modification is found in small quantity in the mother-liquors of the first described nitroparatribromobenzene, melting at 93.5° (p. 179). These liquors still contain a considerable quantity of the last mentioned modification, among the crystals of which are found crusts, and sometimes separate crystals of lighter colour and different form; and on picking these out and recrystallising them several times, first from alcohol and then from a mixture of alcohol and ether, the compound is obtained in transparent nearly colourless rhombic tablets. When heated to 187° , it sublimes in splendid transparent prisms and tablets.

Dinitroparatribromobenzene, $C^6H_2Br_3NO^4$ or $C^6H_2Br_3NO^2.H.NO^2$ or $C^6H_2Br_3NO^2.H$.—This compound, which Mayer obtained in an impure state, is easily prepared by dissolving the mononitro-derivative just described in a mixture of fuming nitric and sulphuric acids, and heating the whole for some time on the water-bath. On pouring the solution into water, drying the resulting precipitate, and crystallising it from a large quantity of boiling alcohol, the dinitro-compound is obtained in yellow-green crystals, melting at 135° (at 125° according to Mayer); and when these crystals, which in the pure state are but very slightly soluble in alcohol, are dissolved in ether, and the solution is left to evaporate very slowly, very large prisms and tablets are obtained, having a pale yellow-green colour, extremely transparent, highly refractive, with an adamantine lustre, and cleaving with great distinctness. Heated with alcoholic ammonia it yields the corresponding dinitrobromophenylenediamine.

It is not yet decided by which of the two formulæ above given the constitution of this dinitro-derivative ought to be represented, but the question might be decided by ascertaining from which of the other two mononitroparatribromobenzenes it might also be prepared. By the action of alcoholic ammonia the dinitro-compound is converted into a dinitro-bromaniline.

2. *Nitro-orthotribromobenzenes*.—Of these there are two varieties represented by the formulæ:



The first modification, $C^6H_3Br_3NO^2$, may be prepared from dibromoparanitraniline, $C^6H_4Br_2NO^2$, in the same manner as the nitroparatribromobenzene melting at 119.5° , is prepared from dibromonitraniline. The product is purified by repeated distillation with vapour of water, and crystallisation from alcohol.

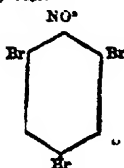
The pure substance, which separates first from the alcoholic solution, forms splendid many-faced crystals, perfectly transparent and nearly colourless. It melts at 112° , and may be sublimed. It is very slightly soluble in cold alcohol, more readily in boiling alcohol, and moderately soluble in ether. Better defined crystals are obtained from a mixture of alcohol and ether.

By reduction, this nitrotribromobenzene is converted into the corresponding tribromaniline, $C^6H_4Br_3$. Heated for ten hours to 120° with alcoholic ammonia, it is converted into ammonium bromide and the dibromoparanitraniline from which it was prepared. A hot mixture of fuming nitric and sulphuric acids converts it into a yellow-green substance—probably a dinitro-1:2:3-tribromobenzene—which melts at 162.4° , and forms with potash a sparingly soluble cinnabar-red salt.

The same mononitro-orthotribromobenzene is formed by the action of ethyl nitrite on the tribromonitraniline obtained by the action of bromine on orthonitro-metabromaniline, and its formation in this manner shows that the tribromonitraniline in question must be represented by the formula $C^6H_3Br_3NO^2$.

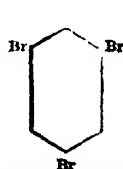
The second modification of nitroorthotribromobenzene, $\text{C}^6\text{H}_2\text{Br}_3\text{NO}_2$, has not yet been obtained with certainty, but is perhaps contained in the product of the action of nitric acid on orthotribromobenzene.

3. *Nitrometatribromobenzene*.—Symmetric tribromobenzene can evidently yield but one mononitro-derivative, viz.:—

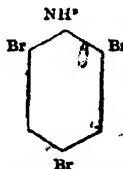


since it is indifferent between which pair of bromine-atoms the nitril-group is introduced. This nitro-derivative is produced:—(1) By boiling symmetric tribromobenzene with fuming nitric acid till the violent evolution of nitrous fumes is over. The product may be precipitated by water, and is easily purified by a few crystallisations from alcohol and ether (O. L. Jackson, *Deut. Chem. Ges. Ber.* viii. 1172). (2) From tribromometanitriline, $\text{C}^6\text{H}_2\text{Br}_3\text{N}$, by substitution of H for NH^2 . A solution of this base in alcohol saturated with nitrous acid is gently heated in a flask connected with a long reflux condenser. A brisk action then takes place, torrents of nitrogen being given off, which carry with them a large quantity of aldehyde. The reaction is completed by adding a further quantity of nitrous ether, and heating for some hours in a water-bath. On distilling off part of the solvent and leaving the remaining solution to cool, the nitrotribromobenzene separates in needle-shaped crystals which may be purified by washing with alcohol and subsequent distillation, under ordinary or greatly reduced pressure, according as the quantity is small or large. Under 11 mm. it distills constantly at 177° (Körner, *Gazz. chim. ital.* iv. 422).

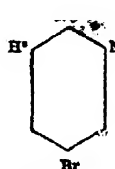
This nitrotribromobenzene forms hard yellowish-white perfectly inodorous rhombic laminar twin-crystals, insoluble in water, sparingly soluble in cold, more easily in warm alcohol, easily soluble in ether, benzene, and carbon sulphide, somewhat soluble in glacial acetic acid (Jackson). It dissolves easily in boiling chloroform, from which it separates on cooling in very large nearly colourless prisms. It melts at 125.1° (Körner) at 124.5° (Jackson). By reduction with tin and hydrochloric acid, it is converted into ordinary tribromaniline, which therefore has the constitution $\text{C}^6\text{H}_3\text{Br}_3$. Heated to 170° in sealed tubes with alcoholic ammonia, it decomposes slowly, with formation of *paranitrobromometadiamidobenzene*, $\text{C}^6\text{H}_2\text{Br}_2\text{N}_2$:—



Nitro-m-tribromobenzene.



Amido-m-tribromobenzene.



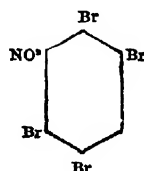
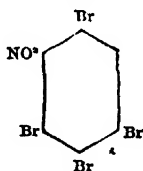
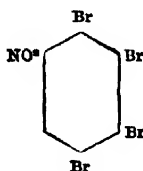
p-nitrobromobenzene.

Dinitrometatribromobenzene, $\text{C}^6\text{H}_2\text{Br}_3\text{NO}_4$.—This compound is formed from symmetric tribromobenzene, according to Körner, by the action of nitric acid of sp. gr. 1.54 (whereby Jackson obtained the mononitro-derivative); according to Jackson by prolonged digestion with a mixture of fuming nitric and strong sulphuric acids. By repeatedly washing the resulting white mass with water, and crystallising from alcohol, it is obtained in shining white needles, melting at 187° (Jackson), at 192° (Körner). It is insoluble in water, sparingly soluble in cold, more readily in hot alcohol, easily soluble in ether, benzene, and carbon sulphide, less soluble in glacial acetic acid than the mononitro-compound.

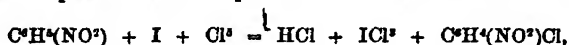
This compound is not attacked by caustic potash, but alcoholic ammonia converts it into sparingly soluble amido-derivatives, which, when treated with potash, yield derivatives of a dibromobenzene, and apparently also of phloroglucin. By heating with a mixture of fuming nitric and sulphuric acids, it is converted into symmetric trinitrotribromobenzene (Körner).

was obtained by A. Mayer and by Riche & Berard by nitration of *tribrom*

as a crystalline substance melting at 86° (1st *Suppl.* 269). V. von Richter (*Deut. Chem. Ges. Ber.* viii. 1427) finds that unsymmetrical tetrabromobenzene 1 : 3 : 4 : 5, or 1 : 2 : 4 : 6 (p. 170), boiled with nitric acid of sp. gr. 1.54, is converted into dinitrotetrabromobenzene; with acid of sp. gr. 1.52 into a mixture of di- and mono-tetrabromobenzene, and with acid of sp. gr. 1.50 into pure mononitrotetrabromobenzene. This compound crystallises from absolute alcohol or benzene in imperfectly developed prisms, which after several recrystallisations melt constantly at 96° . It appears, however, to be susceptible of two modifications differing in their melting points. After fusion in a capillary tube and solidification by rapid cooling, it melts at temperatures much below 90° , sometimes even at 80° ; but the substance thus solidified gradually reverts (in about an hour) to the modification which melts constantly at 96° . A solution of the nitrotetrabromobenzene in a small quantity of boiling absolute alcohol solidifies on cooling to slender needles, which, when left at rest, are converted (with especial quickness in sunshine) into shining laminae melting at 96° . If the needles be quickly dried by pressing between bibulous paper, they melt below 90° – 80° , and exhibit the above-mentioned gradual transformation into the modification melting at 96° . The needles appear, therefore, to consist of the more fusible modification (m.p. about 60°), but they always contain more or less of the higher melting variety. These modifications, however, if really distinct, cannot depend on the relative positions of the bromine and nitryl, as the introduction of the latter group into either of the two vacant places must give rise to the arrangement $\text{C}^{\circ}\text{Br}\cdot\text{Br}\cdot\text{NO}^{\circ}\cdot\text{Br}\cdot\text{H}$. Three nitrotetrabromobenzenes, differing in their mode of orientation, are possible, one formed from each of the three tetrabromobenzenes, viz.:



Nitrochlorobenzenes. *Nitromonochlorobenzene*, $\text{C}^{\circ}\text{H}^{\circ}(\text{NO}^{\circ})\text{Cl}$ (Laubenheimer, *Deut. Chem. Ges. Ber.* vii. 1765; viii. 1621; Beilstein a. Kurbatow, *ibid.* viii. 1417).—Two modifications (α and β) of this compound are formed by the action of nitric acid on monochlorobenzene (2nd *Suppl.* 144). A third is produced by passing chlorine into nitrobenzene mixed with about 10 per cent. of iodine (chlorine alone does not act on nitrobenzene). The gas is readily absorbed, and when a sufficient quantity has been passed into the liquid to form nitrochlorobenzene and iodine trichloride:



the liquid after a while solidifies to a crystalline mass. On agitating this mass with an alkaline solution, washing, and crystallising it from alcohol, pure nitrochlorobenzene is obtained, identical with that which Grieser produced by heating the platinum salt of the diazo-compound obtained from metanitriline with soda.

If the nitrobenzene used in the preparation contains free benzene, hexchlorobenzene is formed at the same time; in this case the product, after washing, must be distilled in a current of steam, and the solidified distillate, which is free from hexchlorobenzene, crystallised from alcohol as above (Laubenheimer).

According to Beilstein a. Kurbatow, a better product is obtained by the use of antimonious chloride. A rapid stream of chlorine is passed through a heated mixture of 200 grams of nitrobenzene and 20 grams of antimonious chloride, and as soon as the weight of the vessel has increased by 62 grams, the contents are washed with hydrochloric acid, water, soda-ley, and again with water. The product is then twice distilled, the portion distilling between 230° and 245° being each time collected apart, and that which boils below 230° is again chlorinated; the portion boiling above 245° soon deposits crystals of hexchlorobenzene. The liquid distilling at 230° – 245° is poured off, cooled, and made to solidify by the introduction of a crystal of pure nitrochlorobenzene; the remaining liquid is drained off, and the dry mass crystallised several times from alcohol.

The nitrochlorobenzene obtained by either of these processes crystallises from a warm alcoholic solution in large yellowish rhombic prisms, in which the axial ratio $a : b : c = 0.5608 : 1 : 0.4975$. Observed combination $\infty P \infty \cdot \infty P \infty \cdot P \infty$. Angle $\infty P : \infty P = 121^{\circ} 28'$; $\infty P \infty : P \infty = 116^{\circ} 27'$; $P \infty : P \infty = 96^{\circ} 51'$. Plane of optic

axes $\propto P \infty$. The axis c is the first median line and negative. A section parallel to the base exhibits the following values of the axial angle in air:

Li=red.	Na=yellow.	Tl=green.
90° 55'	91° 23'	91° 46'

The compound has a strong odour like that of bitter almond oil; sublimes, even at comparatively low temperatures, in very long, flat, shining, flexible needles, melts at 44.2° (corr. 44.4°), and boils under a pressure of 740.7 mm. at 227° (corr. 235.6°). It dissolves easily in ether, benzene, chloroform, carbon sulphide, glacial acetic acid, and hot alcohol, less readily in cold alcohol, and easily forms supersaturated solutions. Being identical with the chloronitrobenzene which Griess obtained from metanitriline, it is itself a meta-compound, and accordingly its melting point is intermediate between those of the two modifications obtained by nitration of chlorobenzene:—

Para.	Meta.	Ortho.
83°.	44.4°.	32.5°.

Metanitrochlorobenzene, boiled with a mixture of fuming nitric and strong sulphuric acids, is converted into chlorodinitrobenzene, $C^6H^4Cl(NO^2)_2$, which forms large thick yellow crystals melting at 38°–39°. Metanitrochlorobenzene, heated with alcoholic potash, yields dichloroxazobenzene, $C^6H^4Cl-N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} N > O$, which crystallises in pale yellow needles melting at 97° (Laubenheimer).

Dinitrochlorobenzenes, $C^6H^4Cl(NO^2)_2$.—(1) *Nitro-orthochloronitrobenzene*, ($Cl : NO^2 : NO^2 = 1 : 2 : 4$), is formed by the action of a mixture of strong nitric and sulphuric acids on ortho- and para-nitrochlorobenzene; also from α -dinitrophenol, ($OH : NO^2 = 1 : 2 : 4$), by the action of PCl^5 . It crystallises in orthorhombic prisms, melting at 50° (Jungfleisch, 2nd Suppl. 145): at 53.4° (Fütig's *Grundriss d. org. Chemie*, 1877, p. 343).

(2) *Nitrometachloronitrobenzene*, $Cl : NO^2 : NO = 1 : 3 : 4$ (Laubenheimer, *Deut. Chem. Ges. Ber.* ix. 760, 768).—This compound is formed by heating metachloronitrobenzene with excess of fuming nitric acid and strong sulphuric acid, and separates, on pouring the product into water, as a yellow oil which, on cooling, solidifies after a while to a crystalline mass having a faint yellow colour. It is somewhat sparingly soluble in cold alcohol, but dissolves easily in hot alcohol and in ether. It is somewhat volatile with vapour of water. Its solutions produce painful blisters on the skin.

Nitro-*m*-chlorobenzene exists in four physical modifications, convertible one into the other; three of them (α, β, γ) are solid, the fourth is liquid.

The α -modification separates on cooling from a solution of the crude product in a small quantity of warm alcohol, at first as an oil, in which needle-shaped crystals form after some time. These may be freed from adhering oil by draining and pressing, and after these operations have been repeated several times, the needle-shaped crystals change into large thick monoclinic prisms, exhibiting the faces $\infty P \infty, \infty P, R \infty, OP$. Cleavage parallel to OP . Twins occur united by $\infty P \infty$. Axial ratio $a : b : c = 1.8873 : 1 : 0.9810$. Angle of inclined axes = 114° 14'.

This modification melts at 36.3°, but gradually passes into the γ -modification (m. p. 38.8°), the transformation being accelerated by pressure or friction, and taking place immediately when a small quantity of the α -modification is melted in a capillary tube and then left to cool.

The β -modification is obtained by immersing a considerable quantity (about 100 grams) of the α -modification contained in a tube in water of 39°–40°, till the whole is fused, then removing it from the water and leaving it to cool. The crystals are monoclinic, with an elongated prismatic development and no perceptible cleavage; hard and brittle. Axial ratio, $a : b : c = 0.6249 : 1 : 0.5600$. Angle of inclined axes = 91° 27'. Observed forms, $\infty P; R \infty; -R \infty$; — P . This modification melts at 37.1°, and gradually passes into the γ -modification (m. p. 38.8°).

The γ -modification is formed, as already mentioned, by transformation of the other two, and likewise separates from the watery liquid into which the oil obtained by heating *m*-nitrochlorobenzene with sulphuric and nitric acids is poured. It crystallises in long thin shining needles belonging to the orthorhombic system, and exhibiting a tolerably distinct cleavage, by which character they are distinguished from the β -modification. From the α -modification they are distinguished by their optical properties. The angles of the optic axes of the two modifications for red, yellow, and green light being as follows:—

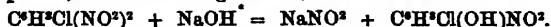
	For Li, red.	Na, yellow.	Tl, green.
	44° 16'	45° 31'	46° 56'
2..	55° 42'	47° 17'	48° 18'

The double refraction in the α -modification is very strong and negative; in the γ -modification moderately strong and positive.

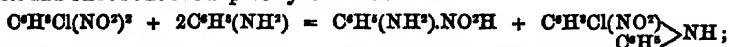
Either of the three crystalline modifications may be obtained at will by introducing a crystal of the desired modification into the fused substance or its ethereal solution. If crystals of two modifications, α and β for example, be introduced simultaneously into the liquid, crystals of both are produced.

Liquid modification.—A modification which remained liquid for many weeks was obtained by immersing capillary tubes containing crystals of the β -modification in a large quantity of water at 42° , and leaving it to cool down gradually to the temperature of the air.

Reactions.—1. Nitrometachloronitrobenzene, heated with soda-ley, yields, as chief product, a chloronitrophenol, $\text{C}^6\text{H}^4\text{Cl}(\text{OH})\text{NO}^2$, which crystallises from water in delicate lemon-yellow prisms, sublimes in long needles, and melts at 38.9° :



2. With aniline at ordinary temperatures, it forms in the first instance aniline nitrite and chloronitrodiphenylamine:



the aniline nitrite then reacts with another molecule of aniline to form diazo-amidobenzene:



and the latter, on subsequent treatment of the product with hydrochloric acid, is transformed into amidazobenzene, $\text{C}^6\text{H}^5.\text{N}^2.\text{C}^6\text{H}^5(\text{NH}^2)$.

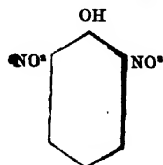
3. Nitrometachloronitrobenzene, boiled with tin and hydrochloric acid, is converted into a chlorophenylene-diamine, $\text{C}^6\text{H}^4\text{Cl}(\text{NH}^2)^2$, which crystallises from water in small colourless laminae melting at 72° , and forms a hydrochloride which gives, with ferric chloride, a deep red liquid and an amorphous dark brown-red precipitate. An attempt to reduce this chlorinated base to the corresponding phenylene-diamine by the action of sodium-amalgam, and thereby determine its constitution, and consequently that of the nitrometachloronitrobenzene from which it is formed, was not successful, the action of sodium-amalgam on it being extremely slow. Considering, however, that this chlorophenylene-diamine reacts with ferric chloride in the same manner as orthophenylene-diamine, that nitro-*m*-chloronitrobenzene is formed by nitration of (1 : 3) chloronitrobenzene: and that, as shown by Wroblevsky (*Deut. Chem. Ges. Ber.* vii. 1060), there is, in most cases of the formation of tri-derivatives of benzene, a marked tendency to the formation of unsymmetrical in preference to symmetrical or consecutive modifications, it appears most probable that the chlorophenylene-diamine in question has the constitution 1 : 3 : 4, or $\text{C}^6\text{Cl.H.NH}^2.\text{NH}^2.\text{H}^2$, and that the nitrometachloronitrobenzene from which it is formed is accordingly $\text{C}^6\text{Cl.H.NO}^2.\text{NO}^2.\text{H}^2$ (Laubenheimer, *Deut. Chem. Ges. Ber.* xi. 768).

Nitrodichlorobenzenes, $\text{C}^6\text{H}^2(\text{NO}^2)\text{Cl}^2$.—*Nitroparadichlorobenzene* (1 : 2 : 5), or $\text{C}^6.\text{NO}^2.\text{Cl.H.H.Cl.H}$, is produced by the action of nitric acid on paradichlorobenzene (2nd Suppl. 145); also, together with metanitrochlorobenzene, by the action of chlorine on mononitrobenzene in presence of antimonious chloride, being gradually deposited from the higher-boiling portions of the product (260° – 260°) in crystals, the separation of which may be facilitated by the introduction of a crystal of the pure substance. Its formation in this last reaction is due to the further chlorination of the metanitrochlorobenzene formed in the first instance, and affords an additional illustration of the fact observed in other instances, that substitution in meta-derivatives takes place in the same manner as in the primary compounds. This monochlorobenzene yields by chlorination paradichlorobenzene, together with a very small quantity of the ortho-modification; and in like manner when metanitrochlorobenzene, $\text{C}^6.\text{Cl.H.NO}^2.\text{H}^2$, is chlorinated, the second atom of chlorine goes into the para-position with regard to the first, the product being (1 : 3 : 4) nitrodichlorobenzene, $\text{C}^6.\text{Cl.H.NO}^2.\text{Cl.H}^2$ (Beilstein & Kurbatow, *Deut. Chem. Ges. Ber.* vii. 1396).

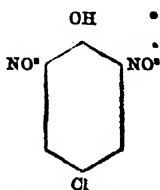
Nitroparadichlorobenzene melts at 55° (B. and K.), at 54.6° , and volatilises easily with vapour of water (Körner). Heated to 165° in sealed tubes with alcoholic ammonia it exchanges an atom of chlorine for NH^2 , and is converted into orthonitroparachloro-aniline, $\text{C}^6.\text{NH}^2.\text{NO}^2.\text{H.Cl.H}^2$. Heated with alcoholic potash, it is converted into tetrachlorazoxybenzene, $(\text{C}^6\text{H}^2\text{Cl}^4)^2\text{N}^2\text{O}$, together with orthonitroparachlorophenol (m. p. 86° – 87°), $\text{C}^6.\text{OH.NO}^2.\text{H.Cl.H}^2$ (2nd Suppl. 912), and a dichloroaniline, $\text{C}^6.\text{NH}^2.\text{Cl.H.Cl.H}^2$, melting at 49.5° , and identical with that which Jungfleisch and Lesimple obtained by treating dichloronitrobenzene with tin and hydrochloric acid (Laubenheimer, *Deut. Chem. Ges. Ber.* vii. 1600).

Nitroparadichlorobenzene, heated with a mixture of fuming nitric and sulphuric acids, is converted into a mixture of two dinitroparadichlorobenzenes, α and β , the former crystallising in faintly yellow laminae, melting at 104.9° , the latter in colourless prisms or flattened needles at 101.3° ; these two modifications may be separated by fractional crystallisation from alcohol, in which the α -modification is less soluble than the β (Körner, *Gazz. chim. Ital.* iv. 350).

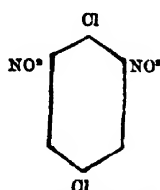
α -Dinitroparadichlorobenzene is analogous in constitution to the dinitrochlorophenol which is obtained by the action of chlorine on β -dinitrophenol, $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{Cl}$ (2nd Suppl. 927), inasmuch as it is converted by fusion with potash into this same dinitrochlorophenol. These three analogous compounds are therefore constituted as follows:—



β -Dinitrophenol.



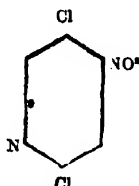
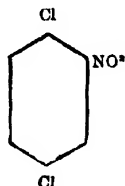
Dinitrochlorophenol.



Dinitroparadichlorobenzene.

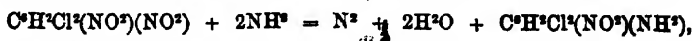
and α -dinitrodichlorobenzene is metadinitroparadichlorobenzene.

For the β -modification of dinitroparadichlorobenzene there remain therefore the two formulæ:—



and at present it does not appear possible to say which of the two represents its actual constitution.

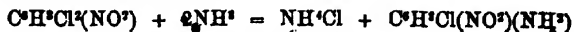
This dinitrodichlorobenzene, heated for some days in sealed tubes to 150° – 160° with alcoholic ammonia, exchanges one of its nitryl-groups for amidogen, and is converted, with elimination of water and nitrogen, into mononitrodichloraniline:



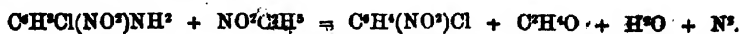
which crystallises in yellow easily sublimable needles melting at 66.4° , and is converted by ethyl nitrite into nitroparadichlorobenzene:



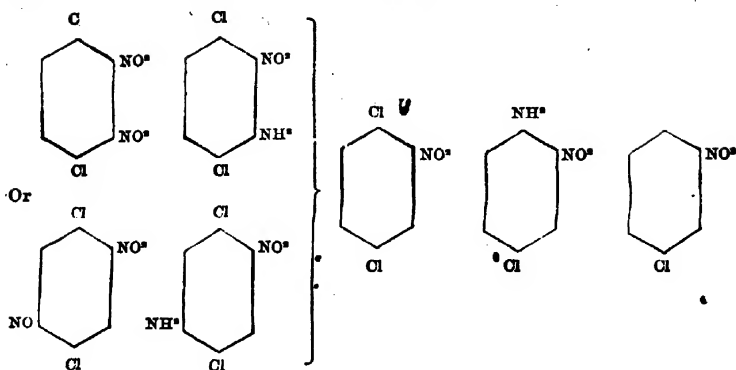
The last body, heated with ammonia for two days in sealed tubes to 150° – 160° , is converted, according to the equation:



into monochloronitraniline, which crystallises from alcohol in spherical groups of deep orange-coloured needles, melting at 116.4° , and perceptibly volatile at ordinary temperatures; and this base, treated in alcoholic solution with ethyl nitrite, is converted into metanitrochlorobenzene, $\text{C}_6\text{H}_4\text{Cl}(\text{NO}_2)$, which crystallises in yellowish prisms or tablets, melting at 48° :



These successive replacements are consistent with either of the two formulæ of dinitroparadichlorobenzene above given, as may be seen from the following diagrams:

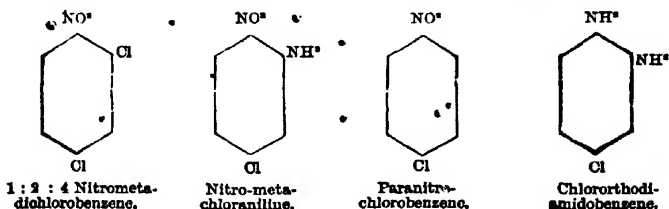


(Körner, *Gazz. chim. ital.* iv. 350).

2. *Nitrometadichlorobenzene*, (1 : 2 : 4), or $C^6H_3Cl_2NO_2$.—Nitric acid of sp. gr. 1.54 acts violently on metadichlorobenzene, forming mononitrometadichlorobenzene, together with other products, the most abundant of which is a dinitro-compound. But by using a more dilute acid (10 pts. acid of sp. gr. 1.54 to 1 pt. water), and assisting the action with a gentle heat, nitrometadichlorobenzene is obtained almost as the only product; and on precipitating and washing with water, and repeatedly crystallising from strong alcohol, this compound is obtained in very long transparent pyramidal needles having a faint yellowish-green colour. It melts at 32.2° , is moderately soluble in cold, very soluble in boiling alcohol, and in all proportions in ether.

With the most concentrated nitric acid, or better in presence of sulphuric acid, it is converted into dinitrometadichlorobenzene, which in the pure state melts at 103° , and crystallises from a mixture of alcohol and ether, in splendid transparent prisms having a faint sea-green tint, and finally, if treated with potash (of the concentration $\frac{1}{2}$) it yields chloride and dinitrometachlorophenate of potassium.

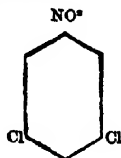
This nitrometadichlorobenzene, heated to 160° in sealed tubes with alcoholic ammonia, is converted into the corresponding nitrometachloraniline, $C^6H_4ClNO_2$, one of the chlorine-atoms being replaced by amidogen; and this base treated with an alcoholic solution of ethyl nitrite is converted, with copious evolution of gas, into paranitrochlorobenzene, $C^6H_4ClNO_2$, melting at 83.3° . The nitrometachloraniline, reduced by tin and hydrochloric acid, yields monochlororthodiamidobenzene, $C^6H_4(NH_2)_2$, which, by prolonged treatment with sodium-amalgam, is converted into Griess's orthodiamidobenzene:



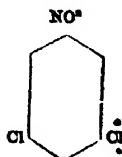
Symmetrical Nitrometadichlorobenzene, $C^6H_3Cl_2NO_2$ (Körner, *Gazzetta*, iv. 376; O. N. Witt, *Deut. Chem. Ges., Ber.* vii. 372; viii. 144).—This modification is prepared by treating dichloroparanitraniline, $C^6H_3Cl_2NO_2$, with nitrous ether in alcoholic solution, distilling off the greater part of the alcohol, precipitating with water, and distilling the precipitated product in a current of steam. To obtain it quite pure, Witt dissolves the distilled product to saturation in warm petroleum-benzin, and exposes the solution to a low temperature. The pure compound then separates out in crystals, while a secondary product, which lowers its melting point, remains in solution.

Symmetrical nitrodichlorobenzene crystallises from boiling alcohol in very long thin

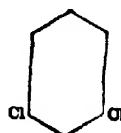
flexible laminae, 5 or 6 mm. broad, melting at 69.4° (Körner); from petroleum-benzin in large prisms melting at 64° – 65° (Vitt). In its other physical and in its chemical properties it resembles the corresponding bromine-derivative, excepting that it dissolves more easily in alcohol. It is not attacked by ammonia, even at the highest temperatures in sealed tubes. Tin and hydrochloric acid reduce it to symmetrical dichloraniline:



Dichloroparanitraniline.



Symmetric Nitrodichlorobenzene.



Symmetric Dichloraniline.

4. *Nitro-orthodichlorobenzene*, (1 : 3 : 4) $C^6H_3Cl_2NO_2$.—Produced, together with an isomeric liquid compound, by the action of nitric acid on orthodichlorobenzene. Long needles melting at 43° (Fittig's *Grundriss der organischen Chemie*, 10te Auflage, 342).

Nitrochlorobromobenzenes (Körner, *Gazetta*, iv. 377). *Nitroparachlorobromobenzene*, $C^6H_3ClBrNO_2$.—The strongest nitric acid acts upon parachlorobromobenzene in the same manner as on paradibromobenzene (p. 176), and the solution, mixed with water, yields a crystalline precipitate, which, when dried and crystallised from alcohol, forms crystals melting at 68.6° , and intermediate in all their properties between nitroparadichloro- and nitroparadibromobenzene. This compound, heated with ammonia in sealed tubes to 160° for ten or twelve hours, is converted into a substance which, in its melting point (111.4°) and other properties closely resembles nitroparabromaniline, $C^6H_4BrNO_2$. It is formed from the nitrochlorobromobenzene by substitution of NH_2 for Cl .

Nitrometachlorobromobenzene, 1 : 3 : 4, or $C^6H_3ClBrNO_2$.—Nitrometachloraniline mixed with nitric acid of sp. gr. 1.38, and subjected to the action of a current of nitrous acid, dissolves almost completely; and the solution mixed with bromine dissolved in aqueous potassium bromide, yields a crystalline diazo-perbromide which, when washed with water, dried, and decomposed by absolute alcohol, yields nitrometachlorobromobenzene, the relative positions of the radicles in which are determined by its mode of formation. The compound, purified by distillation with steam, and repeatedly crystallised from alcohol, is obtained in light yellow green needles, melting at 49.5° . Heated to 160° in sealed tubes with alcoholic ammonia, it is reconverted into nitrometachloraniline.

Another *nitrometachlorobromobenzene*, 1 : 3 : 4 or $C^6H_3BrHClNO_2$, appears to be formed by the action of strong nitric acid on metachlorobromobenzene (m. p. 196°). A violent action takes place in the cold, and on pouring the resulting solution into water, a semifluid mass separates, which soon crystallises, and after repeated crystallisation from alcohol, forms long slightly yellow needles closely resembling nitrometadichlorobenzene, and melting at 46.8° —that is to say, at a temperature exactly intermediate between those of nitrometadichloro- and nitrometadibromobenzene (32.2° and 61.6°). Its analysis showed the presence of chlorine and bromine in equivalent quantities. Heated to 160° in sealed tubes with ammonia, it is converted into a substituted aniline, which separates from alcoholic solution in rather large crystals, resembling those of nitrometachloraniline, excepting that they are rather darker-coloured and less soluble, intermediate in fact in these respects between nitrometachloro- and nitrometabromaniline. Its melting point, 127° , is also the arithmetical mean between those of the same two bases. By analysis it is found to contain 1 at. chlorine and 1 at. bromine to 12 atoms of carbon, whence it would appear to be a mixture in equal numbers of molecules of nitrometachloro- and nitrometabromo-aniline. It cannot, however, be separated into these two compounds, and hence it is rather, perhaps, a mixture of the two bases, $C^6H_3BrHClNO_2$ and $C^6H_3BrHClNO_2$.

This amidated compound is decomposed by ethyl nitrite, and the product purified by distillation with steam and repeatedly crystallised from alcohol, yields a number of compounds, the least soluble of which is paranitrobromobenzene melting at 128.6° , whilst the last mother-liquors deposit large flattened needles melting at 80.3° , and similar in appearance to metanitrochlorobenzene.

Symmetrical Nitrochlorobromobenzene, $\text{C}^6\text{Cl}_2\text{H}_2\text{NO}_2\text{Br}$.—When the bromo-nitroparachloraniline, $\text{C}^6\text{Cl}_2\text{H}_2\text{NO}_2\text{NH}_2\text{Br}$, obtained by treating nitroparachloraniline, $\text{C}^6\text{Cl}_2\text{H}_2\text{NO}_2\text{NH}_2\text{H}$, suspended in strong hydrochloric acid with bromine-vapour (p. 203), is placed in contact with a large excess of ethyl nitrite containing absolute alcohol, it dissolves slowly at ordinary temperatures, the mixture becoming hot, and giving off nitrogen together with vapour of aldehyde. If care be taken to moderate the action, and the ethyl nitrite be kept constantly in excess, a slightly coloured solution will be obtained, from which long flattened needles are deposited on cooling. These, after washing with a little alcohol, may be completely purified by distillation with vapour of water.

The substance thus obtained crystallises in long needles melting at 82.5° , which is not the arithmetical mean between the melting points of symmetrical nitrodichloro- and nitrotribromobenzene. The chlorobrominated derivative resembles these two compounds in its extraordinary resistance to the action of ammonia and other agents.

Nitrochloriodobenzene (Körner, *Gazzetta*, iv. 381). *Nitroparachloriodobenzene*, $\text{C}^6\text{Cl}_2\text{H}_2\text{NO}_2\text{I}$.—Nitroparachloraniline (m.p. 116.4°) mixed with nitric acid of sp. gr. 1.38, and treated with nitrous acid, dissolves quickly, and is converted into a diazo-compound, which, when treated with hydriodic acid, yields a semi-fluid mass, containing the nitrochloriodobenzene, together with free iodine, which must be removed by potash-solution. The remaining substance, washed with water and crystallised from hot alcohol, forms spherical groups of needles, very much like tribromometanitriline. But somewhat lighter in colour. It melts at 63.3° , and may be volatilised without decomposition.

A product, apparently differing from the preceding only in the position of the NO_2 group, is formed by the action of nitric acid of sp. gr. 1.52 on paraiodochlorobenzene dissolved in a large excess of glacial acetic acid.

Nitrometachloriodobenzene, $\text{C}^6\text{Cl}_2\text{H}_2\text{NO}_2\text{I}$.—Nitrometachloraniline, treated in the manner just described, yields a straw-yellow substance which crystallises from a mixture of alcohol and ether in large well-defined prisms melting at 63.4° . It volatilises easily with vapour of water, and dissolves easily in hot alcohol, sparingly in cold.

Another *nitrometachloriodobenzene*, probably $\text{C}^6\text{I}_2\text{H}_2\text{NO}_2\text{H}$, is formed by the action of the strongest nitric acid on metachloriodobenzene. It is somewhat lighter-coloured than the preceding compound, and is distinguished therefrom chiefly by its higher melting point and its crystalline form.

Nitrobromiodobenzene (Körner, *Gazzetta*, iv. 383). *Nitroparabromiodobenzene*, (1 : 3 : 4) or $\text{C}^6\text{Br}_2\text{H}_2\text{NO}_2\text{I}$.—By decomposing with dilute hydriodic acid, the solution of the diazo-compound produced by the action of nitrous acid on a mixture of orthonitroparabromaniline and nitric acid, a product is obtained which, when purified in the manner above described in the case of nitroparachloriodobenzene, melts at 80.4° , has exactly the appearance of *tribrometanitriline*, and has the constitution represented by the formula above given.

Nitrometabromiodobenzene, (1 : 3 : 4) or $\text{C}^6\text{Br}_2\text{H}_2\text{NO}_2\text{H}$.—Produced in like manner by the action of hydriodic acid in large excess on the diazo-compound obtained by passing a strong current of nitrous acid vapour into a mixture of orthonitrometabromaniline and nitric acid of sp. gr. 1.38. The solid product which separates is washed, distilled with aqueous vapour, and purified by crystallisation from alcohol. It is thus obtained in large transparent deep-yellow crystals, quite different in form from those of the compound last described. It melts at 83.5° , and when heated to 180° in sealed tubes with alcoholic ammonia, yields ammonium iodide, together with nitrometabromaniline melting at 151.4° .

Another *nitrometabromiodobenzene*, (1 : 3 : 4), or $\text{C}^6\text{I}_2\text{H}_2\text{BrNO}_2\text{H}$, having the bromine instead of the iodine in the ortho-position with respect to the nitryl, is obtained by gently heating metabromiodobenzene with the strongest nitric acid till it is completely dissolved, and pouring the solution into water. The crystalline precipitate thus obtained is a mixture of at least two compounds, the more abundant of which may be easily separated and purified by repeated crystallisation from strong boiling alcohol, whereas the other, which remains in the mother-liquors, and ultimately separates on concentration in nearly white needles, is difficult to purify. The principal product crystallises from alcohol, on cooling, in lemon-yellow needles melting at 126.8° . By spontaneous evaporation from its solution in a mixture of alcohol and ether, on the other hand, it is obtained in large transparent rectangular tables, of a light orange-yellow colour. It is more soluble in alcohol and in ether than the cor-

responding di-iodo-derivative, and less soluble in these liquids than the dibromo-derivative. Heated to 175° in sealed tubes with alcoholic ammonia, it is transformed into nitrometadiodaniline.

The compound which remains in the mother-liquors, and crystallises as above mentioned in colourless needles, is probably constituted as represented by the formula $C^6H^3NO^2.Br.H^2$.

Nitro-orthobromiodobenzene, $C^6H^3Br.H.NO^2.H^2$.—Paranitro-orthobromaniline treated in the manner described for the preparation of nitro-para-iodobromobenzene from nitro-parabromaniline, yields a product slightly soluble in alcohol, and crystallising from the concentrated solution in large prisms, having a very faint yellowish-green tint, and melting at 106° . Alcoholic ammonia decomposes it very slowly, the reaction requiring many days for its completion, even at 190° ; the product is nitro-orthobromaniline, $C^6H^3NH^2.Br.H.NO^2.H^2$.

The same nitro-orthobromiodobenzene is produced by treating orthobromiodobenzene, $C^6H^3Br.H^4$, with the strongest nitric acid, which dissolves it quickly, without separation of iodine. The solution poured into water gives a precipitate, which, when washed, dried, and crystallised from alcohol, yields, as principal product, a nitro-orthiodobromobenzene melting at 106.1° , and identical with that last described, the mother-liquors retaining products of lower melting point, which have not yet been examined.

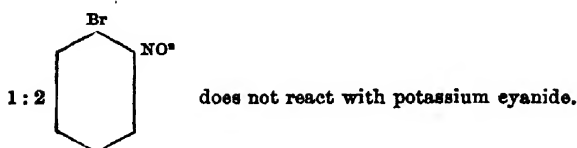
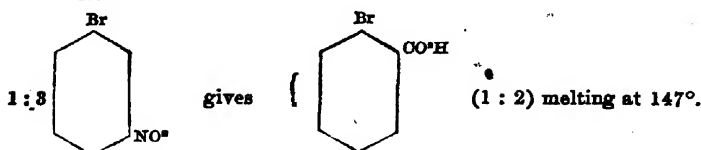
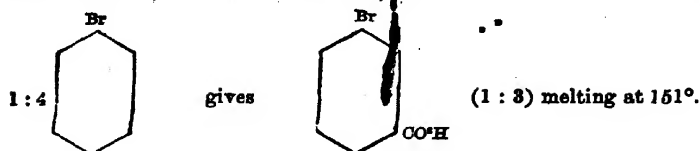
Microdiiodobenzenes, $C^6H^2(NO)^2I^2$. The compound containing the two iodine-atoms in the para-position relatively to one another, cannot be prepared by the action of strong nitric acid on para-iodobenzene, which indeed is thereby decomposed, with separation of 1 atom of iodine, in whatever manner the action may be conducted; both at high and at low temperatures, and with or without the intervention of acetic acid, the products are always free iodine and paranitro-iodobenzene, $C^6H^3NO^2.H.H.I.H^2$.

Nitrometadiiodobenzene, $C^6H^2.H.H.I.NO^2.H^2$.—Metadiiodobenzene, obtained from crystallised metadiodaniline, dissolves very slowly in nitric acid if the acid is heated, of sp. gr. higher than 1.52, and employed in large excess. On pouring the resulting solution into water, nitrometadiiodobenzene separates as an orange-yellow apparently amorphous powder, which may be purified by washing, drying, and solution in boiling alcohol; and the liquid, filtered while hot, deposits the compound on cooling in small scales having the colour of neutral potassium chromate with a faint azure reflex. By spontaneous evaporation, the alcoholic solution deposits the compound in acute quadratic octohedrons, which, if the solution also contains ether, are truncated by the face OP; this face is also more developed as the proportion of ether is greater, the crystals ultimately taking the form of large transparent highly lustrous tablets of a light orange-yellow colour. The compound melts at 168.4° , has a high specific gravity, but is slightly soluble in ether, very slightly in cold alcohol, more easily in hot alcohol. Heated for a few days to 170° with alcoholic ammonia, it yields a yellow-brown solution containing large lance-shaped laminae of nitrometadiodaniline, $C^6H^2.H.NH^2.NO^2.H^2$.

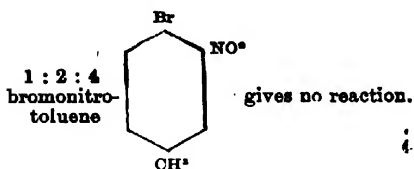
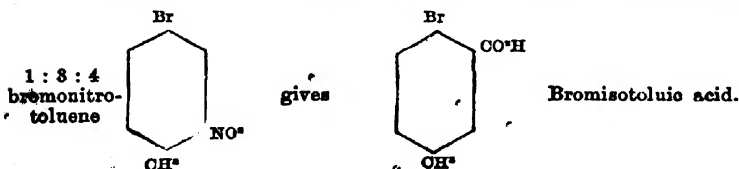
Action of Potassium Cyanide on the Haloid-derivatives of Nitrobenzene (V. v. Richter. *Deut. Chem. Ges. Ber.* iv. 553; vii. 1147; viii. 1418). This transformation, which consists in the replacement of the nitro-group by cyanogen, and the subsequent conversion of the resulting nitril into an acid (replacement of CN by COOH), by boiling with alcoholic potash, takes place with various degrees of facility, according to the number of atoms of Br, Cl, &c., in the molecules and their positions with respect to the NO^2 -group. Thus the replacement of NO^2 by CN takes place in nitromonobromobenzene more easily than in nitrobenzene itself, and still more easily in the nitrodibromobenzenes. With nitroparadibromobenzene (m. p. 84°) it takes place at about 120° , whereas with the nitromonobromobenzenes it requires a temperature of 160° – 180° . The product obtained with nitroparadibromobenzene is a dibromobenzoic acid which crystallises in nacreous flattened needles, melting at 151° , and forming easily soluble barium and calcium salts, $(C^6H^2Br^2.CO^2)^2Ba + 6H^2O$ and $(C^6H^2Br^2.CO^2)^2Ca + 3H^2O$.

In the conversion of the monohaloid-derivatives into aromatic acids by this process, the group CN does not go into the place previously occupied by the NO^2 , but takes up a position one step nearer to the halogen element; consequently the para- and meta-chloronitro-, bromonitro-derivatives, &c., can be converted in this manner into substituted benzoic acids, but the ortho-derivatives cannot; thus:—

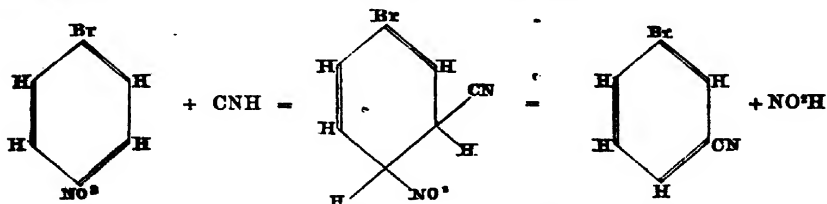
190 BENZENES (NITRO-HALOED), ACTION OF KCy ON.



In like manner with the chloronitrobenzenes and the bromonitrotoluenes :



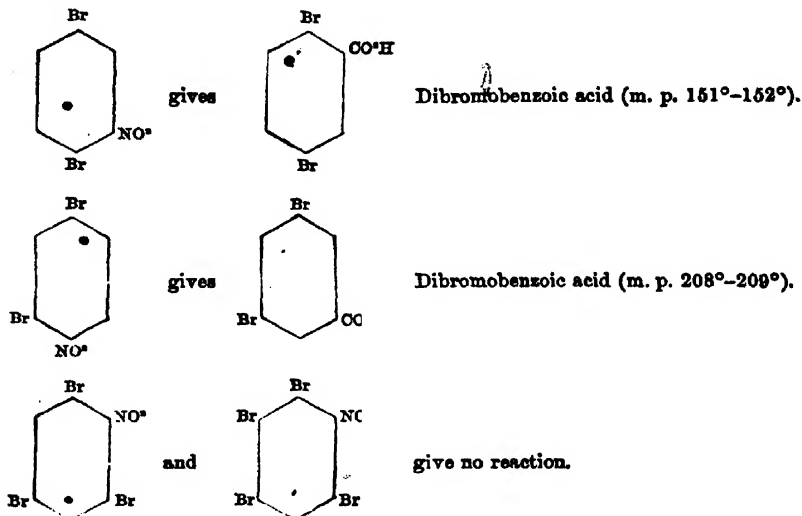
As the CN in these reactions does not go into the place of the NO₂, the change is clearly not one of ordinary double decomposition, but rather one of addition and subsequent partition, perhaps in the following manner. On heating the halonitrobenzene with potassium cyanide and alcohol, an addition of hydrogen cyanide takes place, two doubly linked carbon-atoms of the benzene-ring being partially separated, and the cyanogen-group placing itself near the nitro-group. At the same time the presence of potash determines the separation of nitrous acid (the presence of which may be actually demonstrated), and thereby the normal benzene-ring is re-established :



In the case of a meta-derivative, the mechanism of the reaction may be explained in a similar manner ; in that of an ortho-derivative there is no room for change of place, and therefore the reaction does not occur.

The formation of nitrils in these reactions has not been directly proved; at the high temperature of the reaction indeed (180° – 250°), they appear to be immediately converted into acids by the joint action of potassium cyanide and ammonium carbonate, which is always formed in considerable quantity. The boiling with alkalis after the action of the potassium cyanide may, therefore, in most cases be dispensed with. Sodium cyanide acts in the same way as cyanide of potassium.

With the more highly brominated benzenes, the reaction takes place in a similar manner, whenever there is room for a shifting of the position of the substituted radicle; thus:—



Nitrosobenzene, $C^6H^5(NO)$. When solutions of nitrosyl bromide, $NOBr$, and mercury diphenyl in benzene are mixed, colourless crystals, probably consisting of C^6H^5HgBr , separate out, while the liquid assumes a green colour, and emits a smell of mustard oil:



On distillation a green liquid passes over containing nitrosobenzene, which, however, has not been obtained in the pure state. By treating it with tin and hydrochloric acid it is converted into aniline, and on heating it with aniline acetate, it yields azobenzene. Acids decompose it, hydrochloric acid producing a yellowish-red, and sulphuric acid an intense reddish-violet colour.

Nitrosobenzene is also formed by using nitrosyl chloride instead of the bromide, and instead of benzene, chloroform or carbon sulphide as a solvent. Nitrosyl chloride is best employed in the form of $SnCl_4 \cdot 2NOCl$, which compound is readily obtained in large yellow crystals by passing the vapour of aqua regia over stannic chloride (A. Baeyer, *Deut. Chem. Ges. Ber.* vii. 1638).

Amidobenzenes.—Anilines.

ANILINE. PHENYLAMINE, $C^6H^5NH_2$.—The relative quantities of this base contained in different coal-tar oils have been approximately determined by Watson Smith (*Chem. Soc. J.* [2], xii. 883). Those known as 'light coal-tar oils,' varying in sp. gr. from 0.900 to 1.000, appear to contain aniline in largest quantity and least contaminated with homologous bases. The oils obtained by distilling with caustic soda the black spent acid obtained in the treatment and rectification of crude benzol, are larger in quantity but contain less aniline.

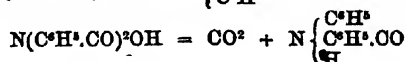
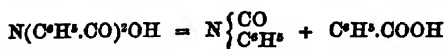
Formation from Dibenzhydroxamic Acid.—Aniline may be obtained from dibenzhydroxamic acid (q.v.) by converting the latter into diphenyl-urea, benzamide or phenyl cyanate, according to the following equations, and decomposing these compounds by the action of acids or alkalis:—

1. Dibenzhydroxamic acid, heated with excess of caustic soda yields benzoic acid

and diphenyl-area, which, when heated with hydrochloric acid, is resolved into carbon dioxide and aniline:



2. Dibenzhydroxamic acid is resolved by distillation into phenyl isocyanate and benzoic acid, which pass over between 160° and 270°, and benzanilide, which remains behind:



Reactions.—1. With *Hypochlorous Acid*.—When chlorine-water, or better, a solution of sodium hypochlorite, is added to a mixture of phenol and aniline, a red colouration is produced, which changes to a deep blue on addition of an alkali. This reaction is not produced either by phenol or by aniline alone. As a test for aniline (in presence of phenol) it is very delicate, being capable of detecting 1 pt. of aniline in 100,000 of water. A similar blue colour is produced by hypochlorites in a mixture of phenol and ammonia, but it is much lighter, and its formation is much less rapid (Jacquemin, *Bull. Soc. Chim.* [2], xx. 68; *J. Pharm. Chim.* [4], xix. 417).

2. With the *chlorides of mono- and trichloracetyl*, aniline yields phenyl-chloracetamide, $N.C^6H^5ClO.C^6H^5.H$, and phenyl-trichloracetamide, $N.C^6H^5Cl^3O.C^6H^5.H$ (Tommasi a. Meldola, p. 6).

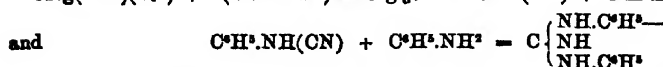
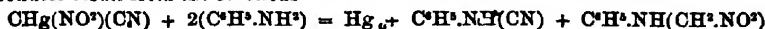
3. Aniline (4 mols.) heated with *dichlorhydrin* (1 mol.) is converted into dianilinehydrin $C^6H^5(C^6H^5.N)^2O$, which crystallises from dilute alcohol in long white needles, easily soluble in dilute acids, but decomposing when the solutions are heated, with formation of aniline and a greasy substance. Its solution in hydrochloric acid gives with *platinic chloride* yellowish-red crystals of the salt, $C^6H^5N^2O.2HCl.PtCl^4$ (Claus, *Deut. Chem. Ges. Ber.* viii. 242).

With *Mercuric Fulminate*.—When aniline is mixed with mercuric fulminate, a rapid action takes place after a while, much heat being evolved, so that with large quantities an explosion may result; if, however, moist fulminate be used, and the aniline be diluted with its own bulk of alcohol, the action is somewhat moderated, although care must be taken to cool the vessel containing the mixture as soon as heat begins to be evolved, *i.e.* in about half an hour. The products are finely divided metallic mercury, and a substance resembling amorphous phosphorus; on treating this with dilute hydrochloric acid, a substance is dissolved which, after crystallisation from the liquid, previously alkalinised with ammonia to remove dissolved mercury, and then again acidified with hydrochloric acid, is neutral, difficultly soluble in cold water, but readily soluble in alcohol, ether, and hot water; it melts at 149°, does not combine with acid or alkalis, and gives the aniline reaction with bleaching powder, together with a smell of chloropicrin on allowing the whole to stand awhile. This body

has the formula $C^6H^5N^2O^2$, and is probably nitromethyl-aniline, $\left. \begin{array}{c} C^6H^5 \\ H \end{array} \right\} N$,
 H

the presence of the NO^2 -group causing the basic properties to disappear.

Besides this product, diphenylguanidine, melting at 146°, is formed; the two products result from the reactions—



cyan-aniline being formed as an intermediate product (Steiner, *Deut. Chem. Ges. Ber.* vii. 1244).

SUBSTITUTION-DERIVATIVES OF ANILINE.

Preparation of Bromo- and Chloro-derivatives (Mills, *Phil. Mag.* [4], xlix. 21).—Aniline dried and purified by cohobation for a few hours with $\frac{1}{4}$ to $\frac{1}{2}$ of its weight of mercuric chloride or bromide, according to the derivative which is to be prepared, is cohobated for some hours with glacial acetic acid; the resulting acetanilide, after being purified by recrystallisation, is powdered, suspended in water, and treated with excess of bromine or chlorine, and the product is heated with powdered potash moistened with spirit. The distillate thus obtained consists chiefly of mono- and di-derivatives.

The actual preparation of acetanilide is, however, unnecessary, as a solution of dry aniline in glacial acetic acid answers equally well. Aniline is dissolved in 2-3 vols. of the acid, and chlorine- or bromine-vapour passed over the surface of the mixture, which must be well agitated. In the case of bromine-vapour the operation is performed in a warm closet, and the bromine is volatilised slowly from a retort, which must be heated by a small flame placed at a considerable distance below, the heat being regulated so that, while vapour comes over freely, no drops of bromine are delivered from the tube of the retort. This tube should be bent vertically downwards, and nearly touch the surface of the aniline mixture in the flask where the operation is conducted. Considerable heat is evolved at first. As the action proceeds, the mixture becomes thicker, and partially solidifies; and at this point the operation must be arrested if a minimum of tri-derivative is required, but continued until total solidification ensues if the tri-derivative is to be a maximum. The whole may, if desired, be submitted to further action by gentle heating with more glacial acetic acid, which dissolves the product. The cooled mass is heated to 100° under water, and afterwards cooled therewith, and the supernatant liquid is filtered off and precipitated with alkali: this precipitate contains mono- and di-derivatives. The insoluble portion is mixed with powdered potash, moistened with spirit, and then heated in order to destroy any traces of aniline that may have been formed. The ratio $\text{C}^{\text{H}}\text{ON} : \text{Br}^{\text{I}}$ furnishes chiefly dibromaniline.

The direct action of chlorine, &c., on aniline itself is not attended with satisfactory results; in presence also of water or aqueous acid there is an enormous amount of by-product.

Separation of the Mixed Derivatives.—The whole is immersed in a very large excess of aqueous hydrochloric acid (1 vol. fuming acid to 9 vols. water), and heated to nearly 100° , with frequent stirring for about an hour in a loosely covered vessel; the whole is then allowed to cool down until the next day. The clear liquid contains only mono- and di-derivatives; the insoluble portion, di- and tri-derivatives. The latter is submitted to repeated hydrochloric treatment as before, until the supernatant clear liquid no longer gives any precipitate with ammonia; it then consists of tri-derivative only—contaminated, however, with some black tarry products. This derivative can be purified by distillation *per se*, or from strong hydrochloric acid or potash-lime. The clear liquids are united and precipitated by ammonia during twenty-four hours, a large excess of ammonia being avoided. The precipitate is then washed, rapidly evaporated with hydrochloric acid to dryness on the water-bath, redissolved (or at any rate well stirred) in hot water, and left to cool thoroughly: the insoluble portion consists of di-derivative, and must be filtered off. The filtrate is again evaporated to dryness and stirred with hot water, &c. Three evaporations to dryness are necessary, and usually sufficient; and the final solution contains mono-derivative only, which yields but an inappreciably small amount of insoluble residue when so evaporated. The mono-derivative may be purified by distillation from aqueous soda in a current of steam; the di-derivative by distillation *per se*, or by *saive* crystallisations from naphtha and spirit.

Bromanilines, $\text{C}^{\text{H}}\text{NH}_2^{\text{Br}}$ (Fittig a. Mager, *Deut. Chem. Ges. Ber.* vii. 1176; viii. 364). *Parabromaniline*, $\text{C}^{\text{H}}\text{NH}_2^{\text{Br}}\cdot\text{H}\cdot\text{H}\cdot\text{Br}\cdot\text{H}^{\text{I}}$.—Obtained by reducing (1 : 4) bromonitrobenzene with tin and hydrochloric acid, distilling the solution after addition of caustic soda, and crystallising from aqueous alcohol; it forms large colourless regular octohedrons, melts at 63° , and cannot be distilled without decomposition. When heated it first melts to a colourless liquid, then suddenly turns violet-blue, and yields a colourless liquid distillate; afterwards crystals collect in the neck of the retort, and there remains a dark-coloured mass which dissolves with blue colour in alcohol. The liquid distillate does not solidify on cooling, but yields, on second distillation, a somewhat considerable quantity of a fluid base boiling at 180° – 190° (probably aniline), after which the above-described phenomena are reproduced. The last mother-liquors obtained in the preparation of parabromaniline contain a small quantity of a base which crystallises in long needles.

Orthobromaniline (1 : 2), prepared in like manner from orthobromonitrobenzene, is a colourless crystalline mass, which melts at 31° – 31.6° , and boils without decomposition at 229° (mercury-column wholly in the vapour). In the preparation of orthobromaniline there is also formed a small quantity of another liquid base which prevents the orthobromanilines from crystallising at ordinary temperatures. The two bases may be separated by means of their hydrochlorides (Fittig a. Mager); see also Hübner a. Alsberg (*Liebig's Annalen*, clvi. 308).

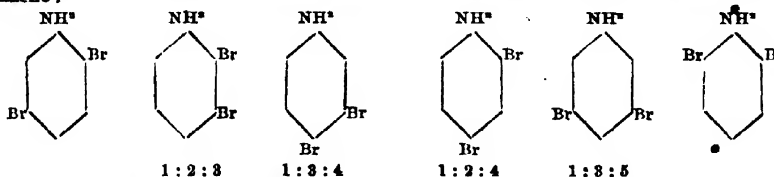
Metabromaniline (1 : 3), obtained by reduction of metabromonitrobenzene, is a colourless crystalline mass which acquires but a very faint tinge of colour on exposure

to light, melts at 18° – 18.5° , boils at 251° , and solidifies immediately after distillation to about 15° (Fittig a. Mager).*

The $\text{C}^6\text{H}^4\text{Br}(\text{NH}^2)\cdot\text{HCl}$, dissolves easily in water, very sparingly in hydrochloric acid, and crystallises in nacreous laminae. The *platinochloride*, $[\text{C}^6\text{H}^4\text{Br}(\text{NH}^2)\cdot\text{HCl}]^2\cdot\text{PtCl}_4$, is a yellow crystalline precipitate (Wurster a. Grubermann).

When nitrous acid is passed into metabromaniline mixed with nitric acid till the whole is dissolved, dilute sulphuric acid then added, and afterwards bromine water, dibromobenzene perbromide separates as an oil, which solidifies over sulphuric acid and lime to a crystalline mass, and is converted by boiling with absolute alcohol into metadibromobenzene (Fittig a. Mager).

Dibromanilines, $\text{C}^6\text{H}^4\text{Br}^2\text{NH}^2$.—Of these compounds there are six possible modifications, one derived from *para*, two from *ortho*, and three from *meta*-dibromobenzene:—



from (1 : 4) $\text{C}^6\text{H}^4\text{Br}^2$

from (1 : 2) $\text{C}^6\text{H}^4\text{Br}^2$

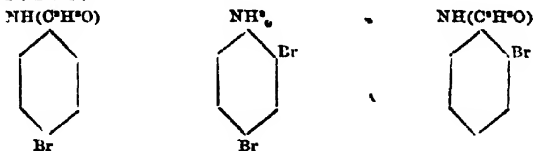
from (1 : 3) $\text{C}^6\text{H}^4\text{Br}^2$

The formulae are analogous to those of the nitro-dibromobenzenes (pp. 176–178), with NH^2 in place of NO^2 .

Of these six modifications, four are known, viz.—1 : 2 : 4, 1 : 2 : 5, 1 : 3 : 4, 1 : 3 : 5, and a fifth which most probably has the structure 1 : 2 : 6.

(1). The modification 1 : 2 : 4 is the ordinary dibromaniline discovered by Hofmann (iv. 436). It is produced: α . By reduction of (1 : 2 : 4) nitrodibromobenzene (Wurster, *Deut. Chem. Ges. Ber.* vi. 491). β . By the action of bromine on acetanilide, or by Mills's method (p. 193). γ . By subjecting parabromacetanilide, $\text{C}^6\text{H}^4\text{NH}(\text{C}^2\text{H}^3\text{O})\cdot\text{H}\cdot\text{H}\cdot\text{Br}\cdot\text{H}^2$ (prepared by the action of acetyl chloride on parabromaniline), finely pulverised and suspended in water, to the action of a current of air charged with bromine vapour, saponifying the product, and distilling it with aqueous vapour (Körner, *Gazzetta*, iv. 329). δ . By a precisely similar series of processes from orthobromacetanilide, $\text{C}^6\text{H}^4\text{NH}(\text{C}^2\text{H}^3\text{O})\cdot\text{Br}\cdot\text{H}^4$ (prepared by the action of acetyl chloride on orthobromacetanilide). As thus prepared, it is contaminated with a small quantity of an isomeric compound, from which, however, it may be freed by crystallisation from alcohol (Körner). ϵ . Together with mono- and tribromaniline, by direct bromination of aniline (Kekulé, 1st *Suppl.* 921). ζ . By the action of alkalis on dibromacetanilide (Fittig, *Grundriss der organischen Chemie*, 10te, Auflage, 356). η . By heating mononitrobenzene with concentrated hydrobromic acid to 185° – 190° , mono- and tribromaniline being formed at the same time (Fittig). θ . By distilling dibromisatin with potash (iv. 435).

The dibromaniline thus obtained boils at 79.4° (Körner), at 79° (Wurster), at 78.82° (Mills). The formation of this dibromaniline from para- and orthobromacetanilide shows that it has the NH^2 -group in the para-position with regard to one of the bromine-atoms, and in the ortho-position with regard to the other, its constitutional formula being 1 : 2 : 4:—



The two bromine-atoms are therefore in the meta-position with regard to each other; and this conclusion is corroborated by the fact that the dibromaniline, when treated with ethyl nitrite, is converted, by substitution of H for NH^2 , into meta-dibromobenzene.

(2). The modification 1 : 2 : 5, discovered by Riche a. Bérard (*Compt. rend.* lix. 141; *Institut.* 1864, 262) is prepared by adding paradibromobenzene to fuming nitric

acid, and reducing the resulting nitro-compound, $C^6H_5NO_2.Br.H.H.Br.H$, with ammonium sulphide, or better, with tin and hydrochloric acid. The dibromaniline separated from the hydrochloride by lime, and purified by rectification, dissolves easily in alcohol and ether, and crystallises in nodular groups of prisms having a silky lustre, and melting at 51° – 52° (V. Meyer a. O. Stüber, *Liebig's Annalen*, clxv. 179).

(3). The modification 1 : 3 : 4, obtained by reduction of the corresponding nitro-dibromobenzene (p. 178), forms colourless crystals melting at 80.4° (Körner, *Gazzetta*, iv. 370). This modification and the next are much more strongly basic than the two previously described.

(4). *Symmetric Dibromaniline*, (1 : 3 : 5), is prepared by reducing symmetric nitro-dibromobenzene (p. 177) with tin and hydrochloric acid, supersaturating the product with potash, and distilling in a current of steam. It then passes over as a liquid which crystallises in white needles melting at 56.5° . It is a somewhat powerful base. The hydrochloride crystallises in flattened needles, which may be recrystallised from water containing a little hydrochloric acid, but it is partially decomposed by a large quantity of pure water. Ethyl nitrite added in excess, and mixed with alcohol, acts strongly on this dibromaniline, converting it into metadibromobenzene. The substitution of bromine (by the diazo-reaction) for the NH^2 of this base converts it into symmetric tribromobenzene (Körner, *Gazzetta*, iv. 368).

(5). A fifth dibromaniline, probably 1 : 2 : 6, is formed by the action of bromine on orthobromaniline, or by brominating ortho-acetobromanilide (p. 4) and eliminating the acetyl-group with potash. Now when the dibromaniline thus obtained is treated with an alcoholic solution of nitrous ether, so as to remove the NH^2 -group, a dibromobenzene is obtained which, after washing and rectification, forms a limpid liquid boiling at 215° (uncorr.) and not solidifying in a freezing mixture: therefore *meta*-dibromobenzene. Hence it follows that the dibromaniline must have its two bromine-atoms in the meta-position; and since, from its mode of formation, one of these bromine-atoms must be in the position 2, its formula must be either 1 : 2 : 4, or 1 : 2 : 6. Now it does not appear to be ordinary dibromaniline (though its physical properties are not described), so that there remains for it only the formula 1 : 2 : 6 (Meyer a. Stüber, *Liebig's Annalen*, clxv. 161).

Tribromanilines, $C^6H_3Br_3.NH^2$.—Of six possible modifications, only two are known, viz. :—

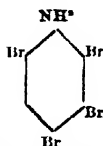
α (1 : 2 : 4 : 6).^{*} This is the ordinary modification formed by the action of bromine in excess on aniline (iv. 436), and on ortho- or parabromaniline; also by reduction of (1 : 2 : 4 : 6) nitro-bromobenzene with tin and hydrochloric acid (Körner), and, together with aniline and dibromaniline, by dry distillation of parabromaniline (Buchner, *Deut. Chem. Ges. Ber.* viii. 361). It crystallises in long colourless needles; melts at 118° ; does not unite with acids. By the action of nitrous ether, the amido-group is eliminated, and the tribromaniline is converted into symmetrical tribromobenzene (Meyer a. Stüber, *Liebig's Annalen*, clxv. 173).

β (1 : 3 : 4 : 5).^{*} This modification, formed by reduction of the corresponding nitrotribromobenzene, is also crystalline, does not melt at 130° , appears to decompose at a higher temperature; forms salts with acids. By decomposition with ethyl nitrite, it yields consecutive tribromobenzene (Körner, *Gazzetta*, iv. 328).

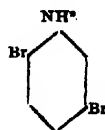
Tetrabromaniline, $C^6HBr_4.NH^2$.—Of three possible modifications of this compound, (1 : 2 : 3 : 4 : 5), (1 : 2 : 3 : 5 : 6), and (1 : 2 : 3 : 4 : 6) or (1 : 2 : 4 : 5 : 6), NH^2 in 1, only the third is at present known. It is formed by the action of bromine in excess on metabromaniline and on (1 : 2 : 5) or (1 : 3 : 6) dibromaniline (amido-paradibromobenzene). Its constitution is therefore represented by the formula 1 : 2 : 3 : 4 : 6 :—



Metabromaniline.



Tetrabromaniline.



(1 : 3 : 6) Dibromaniline.

After repeated crystallisation from boiling alcohol containing a small quantity of toluene, it forms long colourless needles having a silky lustre and melting at 116.3° (Körner); at 116° – 117° (Wurster a. Nölting). When heated in small quantity, it

* NH^2 in 1.

sublimes without decomposition in transparent vitreous needles or prisms melting at the same temperature. When gradually added to a mixture of absolute alcohol and alcohol saturated with nitrous acid, it dissolves with rise of temperature and evolution of nitrogen, and the solution deposits a pasty mass of needle-shaped crystals which, after being heated for some time with ethyl nitrite in a flask with reversed condenser, then washed, dried, and distilled, yields unsymmetrical tetrabromobenzene (p. 170) (Körner, *Gazzetta*, iv. 328; Wurster a. Nölting, *Deut. Chem. Ges. Ber.* vii. 1864).

Pentabromaniline, $C^6Br^5.NH^2$, is formed by passing bromine-vapour to saturation into a large quantity of water slightly acidulated with hydrochloric acid, and containing in suspension the hydrochloride of symmetric dibromaniline (p. 195). A bulky white precipitate is thereby formed, which may be washed with water, and purified by solution in a mixture of 1 vol. absolute alcohol and 2 vols. toluene; pure alcohol at boiling heat dissolves it only in very small quantity. The pentabromaniline crystallises on cooling in large transparent needles, having an almost adamantine lustre, and not melting at 222°. It is not perceptibly attacked by ethyl nitrite at ordinary pressure and temperature (Körner, *Gazzetta*, iv. 368).

On *Acetobromanilides*, see *ACETANILIDE* (p. 4).

Chloranilines (mono-). (Beilstein a. Kurbatow, *Liebig's Annalen*, cxxxvi. 27; *Deut. Chem. Ges. Ber.* vii. 1395.) **Parachloraniline**, $C^6.NH^2.H.H.Cl.H^2$ (described in iv. 438 as the α -modification) is most readily obtained by reducing *p*-nitrochlorobenzene with tin and hydrochloric acid. When the reaction is over, the liquid is diluted with water and distilled with excess of quick lime, and the base which passes over is freed from traces of adhering oil by dissolving it in hydrochloric acid, and again distilling with lime. Parachloraniline forms colourless rhombic prisms of 93° 62', melts and sublimes at 70°–71°, and boils at 230°–231°. [The chloraniline obtained by Mills from acetanilide (p. 193) boils at 69°–69°, and is doubtless therefore the para-modification.] The salts of parachloraniline are moderately stable, being but slightly decomposed by boiling with water. Their aqueous solution has an acid reaction. The *hydrochloride*, $(C^6H^4ClN).H^2SO^4$, separates from solution by spontaneous evaporation in very fine large crystals. The *sulphate*, $(C^6H^4ClN)^2.H^2SO^4$, forms shining laminae, very slightly soluble in cold water. The *nitrate*, $C^6H^4ClN.HNO^3$, forms broadly laminar crystals, almost always having a faint rose colour. A hundred pts. of water at 12.5° dissolve 6.74 pts. of this salt.

Metachloraniline, $C^6.NH^2.H.Cl.H^2$, prepared by reduction of metachloronitrobenzene, is a liquid boiling at 230° (bar. 767.3 mm.; thermometer in the vapour), and having a sp. gr. of 1.2432 at 0°. It is a moderately strong base. Its salts are moderately stable, being but partially decomposed by boiling with water. The *hydrochloride*, $C^6H^4ClN.HCl$, crystallises in shining laminae, very soluble in water and in alcohol of 90 per cent. The *nitrate*, $C^6H^4ClN.HNO^3$, forms broad lanceolate crystals, of a light rose colour, slightly soluble in cold water, easily in hot water, and in alcohol of 90 per cent. The *sulphate*, $(C^6H^4ClN)^2.H^2SO^4$, crystallises in thick short needles, very slightly soluble in cold, much more easily in boiling water, somewhat soluble in boiling alcohol.

Orthochloraniline, $C^6.NH^2.Cl.H^4$, may be prepared by the action of tin and hydrochloric acid on liquid chloronitrobenzene, freed by decantation from the greater part of the solid modification. The two bases thereby produced may be partially separated by fractional distillation in a current of steam, the orthochloraniline, which is liquid, passing over first, so that the latter portions of the distillate solidify in the condensing tube. To separate them completely, the more volatile liquid portion of the distillate is neutralised with sulphuric acid and distilled with water. The sulphate of orthochloraniline is thereby decomposed, the base distilling over, while the parachloraniline sulphate remains behind. The orthochloraniline may be further purified by crystallising its hydrochloride from dilute hydrochloric acid. Small quantities of the two bases may be separated by dissolving them in alcohol, adding the exact quantity of picric acid required to combine with them, and crystallising from alcohol or benzene, in which the ortho-picrate is much less soluble than the para-salt.

Orthochloraniline is a liquid having a sp. gr. of 1.2338 at 0°, remaining fluid at –14°, and boiling at 207°. Its salts are easily decomposed by boiling with water. The *hydrochloride*, $C^6H^4ClN.HCl$, forms large transparent rhombic plates; 100 pts. of water at 15.2° dissolve 11.96 parts of it. The *nitrate*, $C^6H^4ClN.HNO^3$, separates, on addition of nitric acid to an alcoholic solution of the base, in reddish needles. 100 pts. water at 13.5° dissolve 10.2 parts of it. The *sulphate* forms needles very soluble in water.

Dichloranilines, $C^6H_4Cl^2NH^2$.—Of these bodies there are six possible modifications, analogous to the dibromanilines (p. 194). Five have been obtained, viz. (NH^2 in 1):—

1 : 2 : 3	1 : 3 : 4
1 : 2 : 4	1 : 3 : 5
1 : 2 : 5	

They may all be formed by reduction of the corresponding nitrodichlorobenzenes.

(1 : 2 : 3), produced by reduction of nitro-orthodichlorobenzene, $C^6H_3Cl^2Cl.H^3$, melts at 23° – 24° , boils at 252° , yields an acetyl-derivative melting at 156° – 157° , and is convertible, by the diazo-reaction, into consecutive trichlorobenzene (Beilstein a. Kurbatow, *Deut. Chem. Ges. Ber.* x. 711).

(1 : 2 : 4).—This is the ordinary modification which Hofmann obtained by boiling dichlorisatin with potash (iv. 440); but it is more easily prepared, as shown by Griess (*ibid.*)⁹ from acetodichloranilide. O. N. Witt (*Deut. Chem. Ges. Ber.* vii. 1601) passes chlorine-gas into water in which acetanilide is suspended, washes the yellow greasy product with ice-cold alcohol, crystallises it from boiling alcohol, decomposes the dichloracetanilide thus purified (m. p. 140°) by boiling with hydrochloric acid, and precipitates the resulting dichloraniline with ammonia. An easier mode of preparation, according to Beilstein a. Kurbatow (*ibid.* 176) is to dissolve 100 grams of acetanilide, with aid of heat, in a mixture of 525 cc. glacial acetic acid, and 350 grams of water, and pass into the solution the quantity of chlorine theoretically required to form acetodichloranilide. The liquid then becomes darker and deposits acetodichloranilide mixed with a small quantity of acetomono-chloranilide. The precipitate is decomposed by boiling with alkali, and the dichloraniline thereby obtained is freed from admixed mono-chloraniline by dissolving it in warm, moderately strong hydrochloric acid, evaporating to dryness, and treating the residue with hot water, which dissolves the hydrochloride of mono-chloraniline, leaving the dichloraniline undissolved.

Dichloraniline (1 : 2 : 4) dissolves easily in alcohol, and crystallises therefrom in beautiful needles. From water, in which it is but slightly soluble, it separates in flat shining very flexible needles melting at 62.5° , and boils without decomposition at 239° (Witt). According to Beilstein a. Kurbatow, it crystallises from weak spirit in long silky needles, melts at 63° , and boils at 245° (thermometer in the vapour). The hydrochloride, $C^6H_4Cl^2N.HCl$, crystallises from solution in hydrochloric acid in stellate groups of highly lustrous needles, decomposed by water into hydrochloric acid and the free base.

(1 : 2 : 5) or (1 : 3 : 6).—This modification is formed by reduction of $C^6H_3Cl^2Cl.H.H.Cl.H$, and, together with (1 : 3 : 4) dichloraniline and two trichloranilines, by chlorination of metachloraniline. It forms colourless needles melting at 50° (Beilstein a. Kurbatow, *Deut. Chem. Ges. Ber.* ix. 1888).

(1 : 3 : 4).—Formed, as above-mentioned, by chlorination of (1 : 3) chloraniline; also by reduction of (1 : 3 : 4) nitrodichlorobenzene. It is crystalline, melts at 71.5° , and boils at 272° .

(1 : 3 : 5).—*Symmetrical Dichloraniline*.—This modification, formed by the action of tin and hydrochloric acid on (1 : 3 : 5) nitrodichlorobenzene, crystallises from water, in which it is moderately soluble, in long white brittle needles melting at 50.5° . It is decomposed by nitrous ether, with evolution of nitrogen, and on adding water to the resulting solution, metadichlorobenzene separates in drops. The acetyl-derivative forms radiate groups of needles and dissolves readily in alcohol (O. N. Witt, *Deut. Chem. Ges. Ber.* viii. 143).

Trichloranilines, $C^6H_3Cl^3NH^2$.—Two modifications are known, viz.—1 : 2 : 4 : 5 and 1 : 2 : 4 : 6.

(1 : 2 : 4 : 5) trichloraniline is formed by reduction of the corresponding nitrotrichlorobenzene with tin and hydrochloric acid. It crystallises in colourless needles, melts at 96.5° , and boils at 270° (Lesimple, 1st *Suppl.* 921).

1 : 2 : 4 : 6 is the ordinary modification which Hofmann obtained by the action of chlorine on aniline or mono-chloraniline (iv. 441). Beilstein a. Kurbatow (*Deut. Chem. Ges. Ber.* viii. 1655) prepare it by passing chlorine into a solution of 100 pts aniline in acetic acid until the weight has increased by 229 parts. On adding water a precipitate is formed, which is distilled with soda, and the distillate boiled, first with weak and then with strong hydrochloric acid. This trichloraniline crystallises from petroleum-naphtha in long brilliant needles, and dissolves readily in alcohol, ether, and carbon sulphide, less freely in dilute acetic acid. It melts at 77.5° , and boils at 260° . Nitrous acid converts it into symmetric trichlorobenzene.

Iodanilines, $C^6H_4I.NH^2$. The ortho-modification is unknown: the meta- and para-modifications are formed by reduction of the corresponding nitro-iodobenzenes.

Meta. Silvery laminæ melting at 25°. *Para.* Colourless needles melting at 60°. The latter is also formed by the action of iodine on aniline. (Compare iv. 444, and 1st Suppl. 921, where, however, the prefix *para* is applied to the modification now called *meta*.)

Nitraniilines, $C^6H^4(NO^2)_2NH^2$. *Ortho- and Paranitraniiline.*—Both these modifications are produced by treating acetanilide with fuming nitric acid, and distilling the resulting nitro-acetanilide with potash. Paranitraniiline was thus obtained by Arppe (iv. 445), and has hitherto been supposed to be the only product formed by this reaction. Körner, however, finds that the product likewise contains the ortho-modification, which Walcker a. Zincke first obtained by the action of alcoholic ammonia on orthonitro-bromobenzene.* The quantity of orthonitraniiline formed increases with the strength of the acid, which, however, must not exceed sp. gr. 1.466, as otherwise the mixture is apt to take fire, even if cooled by ice. The acid of sp. gr. 1.464—1.466, freed from lower oxides of nitrogen, is placed, in quantities of about 20 grams, in small beakers surrounded by ice, and 6 grams of pulverised acetanilide is introduced *en masse* into each beaker. When the very violent reaction which occurs is over, the product is added to pounded ice, then rapidly filtered, washed with ice-cold water, and quickly introduced into an excess of a strong potash-ley. The mixture of nitraniilines thus formed is submitted to distillation in a current of superheated steam until the distillate ceases to have an orange-red colour; the orthonitraniiline then separates from the distillate in beautiful orange-yellow needles, melting at 71.5°, and exhibiting all the properties ascribed to it by Zincke. In successful operations as much as 14 or 16 per cent. of the acetanilide is obtained in the form of orthonitraniiline. Orthonitraniiline may also be obtained by reducing orthodinitrobenzene with ammonium sulphide.

Paranitraniilins (1 : 4) is obtained from the residue of the distillation by boiling with water, and filtering hot, and may be decolorised by recrystallisation from boiling water in presence of a small quantity of animal charcoal, after the adhering potash has been neutralised with hydrochloric acid. It crystallises in large laminæ having a lemon-yellow colour, with azure reflex, and melts at 145.9°.

Metanitraniiline (1 : 3), obtained by partial reduction of pure metadinitrobenzene (m. p. 89.8°), melts at 109.9°. Metadinitrobenzene is much more easily reduced to nitraniiline than the corresponding ortho-compound.

Dinitranilines, $C^6H^3(NO^2)_2.NH^2$.—The unsymmetrical modification 1 : 2 : 4 (NH^2 in 1) was discovered by Gottlieb (iv. 447), who obtained it by the action of alkalis on dinitrophenyl-citraconimide or dinitrocitraconanil, $C^6H^3(NO^2)_2.N(C^2H^4O^2)$, or on dinitro-acetanilide, $C^6H^3(NO^2)_2.N(C^2H^3O)$. It was afterwards obtained by Clemm (*J. pr. Chem.* [2], i. 145) from the corresponding dinitrochlorobenzene (m. p. 50°, b. p. 316°) by heating with alcoholic ammonia. In like manner it may be formed from the corresponding dinitrobromo- or dinitroiodobenzene; also by heating dinitranisol (the methylic ether of (1 : 2 : 4) dinitrophenol) with aqueous ammonia to 100° for three or four hours (H. Salkowski, *Deut. Chem. Ges. Ber.* v. 872; vi. 130). It crystallises in light yellow prisms melting at 182°–183°; dissolves in 132 pts. alcohol at 21°; does not combine with acids. By reduction with tin and hydrochloric acid it is converted into triamidobenzene; by the action of nitrous acid on its alcoholic solution, into metadinitrobenzene (Salkowski).

The consecutive modification (1 : 2 : 6) obtained by heating the methylic or ethylic ether of (1 : 2 : 6) dinitrophenol with aqueous ammonia, forms long dark yellow needles melting at 138°, soluble in 192 pts. of alcohol at 21°, and only slightly soluble even in hot alcohol. Heated to 120° for several hours with absolute alcohol saturated with nitrous acid, it yields metadinitrobenzene, and a compound melting at 119°, probably trinitrobenzene (Salkowski a. Rehs, *Deut. Chem. Ges. Ber.* vii. 370).

The existence of these two dinitranilines, and of the corresponding dinitroiodobenzenes, &c., containing the two nitro-groups in the same position (*meta*) affords additional proof that the substituted radicles in di-derivatives of benzene belonging to the series which includes ordinary dinitrobenzene and resorcin, cannot be in the relative position 1 : 4, as formerly supposed (Körner, *Gazzetta*, iv. 324; see further 2nd Suppl. 924).

Trinitranilins, $C^6H^2(NO^2)_3.NH^2$ (1 : 2 : 4 : 6).—*Picramide.*—This compound, discovered by Pisani (iv. 443), is obtained by the action of alcoholic ammonia on trinitrochlorobenzene, $C^6Cl.NO^2.H.NO^2.H.NO^2$, or trinitrophenyl chloride (chloropieryl) or on the ethylic or methylic ether of picric acid. It crystallises from alcohol in thick yellow plates having a beautiful blue shimmer, and melting at 188° (Liebermann a. Palm, *Deut. Chem. Ges. Ber.* viii. 278). When treated with tin and hydrochloric acid

* Compare 2nd Suppl. 944, where, however, the prefixes *ortho* and *para* are used in the sense contrary to that now assigned to them.

it yields, not tetramidobenzene as might be expected, but in consequence of oxidation which takes place during the reaction, a base which appears to have the composition $C^6H^2\{(NH^2)^4\}$ or $C^6H^2\{(OH)^2\}$. This base has not been obtained in the free state: its hydrochloride and sulphate have respectively the formulæ $C^6H^2N^2O^2.2HCl$, and $C^6H^2N^2O^2.H^2SO^4$ (H. Salkowski, *Deut. Chem. Ges. Ber.* vi. 139).

Action of Picryl Chloride on the Nitranilines.—Metanitraniline and picryl chloride act on one another when dissolved in boiling absolute alcohol, with formation of *para-picryl metanitraniline*, $N \begin{Bmatrix} C^6H^2(NO^2)^{\mu} \\ C^6H^2(NO^2)^{\pi} \\ H \end{Bmatrix}$ (where μ , π , and ω indicate respectively

meta, para, and ortho); this compound crystallises from glacial acetic acid in small orange-yellow transparent crystals, melting at 205° , and insoluble in water and ether, and only slightly soluble in boiling absolute alcohol. Similarly *para-picryl-paranitraniline*, $N \begin{Bmatrix} C^6H^2(NO^2)^{\pi} \\ C^6H^2(NO^2)^{\omega} \\ H \end{Bmatrix}$, melting at 216° , is formed when picryl chloride acts on paranitraniline; this compound closely resembles the previously described isomeride, but is slightly more soluble in most solvents. On nitration these two bodies furnish respectively *para-picryl-metapicrylamine* and *dipara-picrylamine*, $N \begin{Bmatrix} C^6H^2(NO^2)^{\mu} \\ C^6H^2(NO^2)^{\pi} \\ H \end{Bmatrix}$, and

$N \begin{Bmatrix} C^6H^2(NO^2)^{\pi} \\ C^6H^2(NO^2)^{\omega} \\ H \end{Bmatrix}$, melting at 261° and 235° respectively, and exploding violently when heated; para-picryl-metapicrylamine regenerates para-picryl-metanitraniline when water is added to its solution in glacial acetic acid.

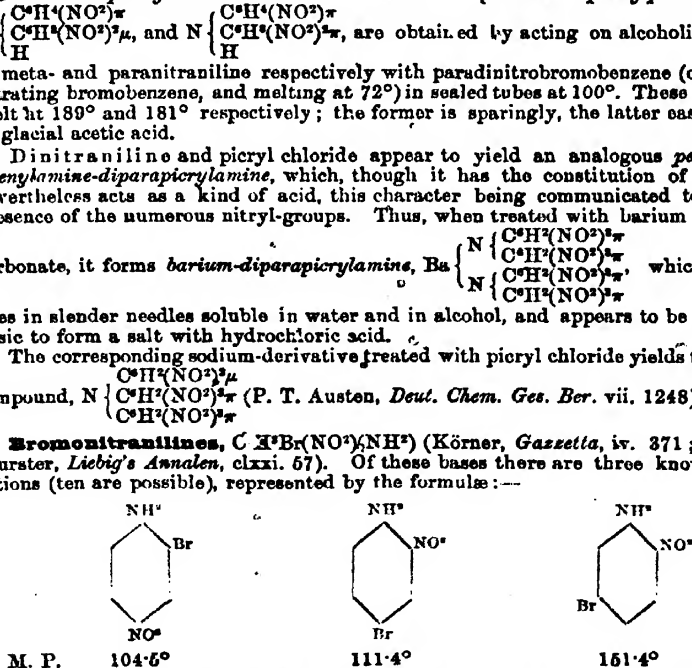
Paradinitrophenylmetanitraniline and *paradinitrophenylparanitraniline*, $N \begin{Bmatrix} C^6H^2(NO^2)^{\pi} \\ C^6H^2(NO^2)^{\mu} \\ H \end{Bmatrix}$, and $N \begin{Bmatrix} C^6H^2(NO^2)^{\pi} \\ C^6H^2(NO^2)^{\omega} \\ H \end{Bmatrix}$, are obtained by acting on alcoholic solutions of meta- and paranitraniline respectively with paradinitrobenzene (obtained by nitrating bromobenzene, and melting at 72°) in sealed tubes at 100° . These compounds melt at 189° and 181° respectively; the former is sparingly, the latter easily soluble in glacial acetic acid.

Dinitraniline and picryl chloride appear to yield an analogous *pentanitrodi-phenylamine-dipara-picrylamine*, which, though it has the constitution of an amine, nevertheless acts as a kind of acid, this character being communicated to it by the presence of the numerous nitryl-groups. Thus, when treated with barium hydrate or carbonate, it forms *barium-dipara-picrylamine*, $Ba \begin{Bmatrix} N \begin{Bmatrix} C^6H^2(NO^2)^{\pi} \\ C^6H^2(NO^2)^{\pi} \\ N \end{Bmatrix} \\ C^6H^2(NO^2)^{\pi} \end{Bmatrix}$, which crystal-

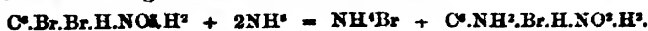
lises in slender needles soluble in water and in alcohol, and appears to be sufficiently basic to form a salt with hydrochloric acid.

The corresponding sodium-derivative treated with picryl chloride yields the tertiary compound, $N \begin{Bmatrix} C^6H^2(NO^2)^{\mu} \\ C^6H^2(NO^2)^{\pi} \\ C^6H^2(NO^2)^{\pi} \end{Bmatrix}$ (P. T. Austen, *Deut. Chem. Ges. Ber.* vii. 1248).

Bromonitranilines, $C^6H^2Br(NO^2)(NH^2)$ (Körner, *Gazzetta*, iv. 371; Meyer a. Wurster, *Liebigs Annalen*, cxlxi. 57). Of these bases there are three known modifications (ten are possible), represented by the formulæ:—



(1). *Orthobromoparanitraniline*, $(NH^2 : Br : NO^2 = 1 : 2 : 4)$, is formed by heating the corresponding nitrodibromobenzene (m. p. 58.6°) to 180° – 190° in sealed tubes for several hours with a large excess of alcoholic ammonia:



To separate the base, the greater part of the alcohol is distilled off, the remaining liquid is mixed with water, and the copious precipitate thereby formed is crystallised from boiling water, or better from weak spirit. From the latter solution the base crystallises in slender canary-yellow needles melting at 104.5° . With strong hydrochloric acid it forms a crystalline hydrochloride, which dissolves but slightly in the strong acid, and is decomposed by water.

The base dissolved in nitric acid and treated with nitrous acid, is quickly converted into the corresponding diazo-compound, the perbromide of which, when decomposed by alcohol, yields the original nitrodibromobenzene. The diazo-compound is converted by hydriodic acid into nitro-orthodibromobenzene.

The following reactions determine the constitution of the base:—1. It dissolves easily in ethyl nitrite mixed with a little alcohol, forming a solution which, when freed by distillation from alcohol and unaltered nitrous ether, gives with water an oily precipitate, exhibiting, when purified by distillation with steam, the characters of *meta*-nitrobromobenzene, $C^6H_4NO^2.H.Br.H^2$.

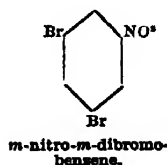
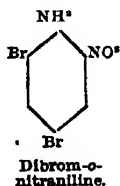
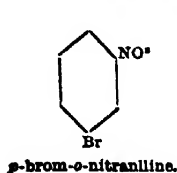
2. With reducing agents, it yields a bromodiamidobenzene, which, when treated with sodium-amalgam, is converted, by exchange of Br for H, into *para*-diamidobenzene, $C^6H_4.NH^2.H.H.NH^2.H^2$, yielding quinone by oxidation.

3. On passing air saturated with bromine through its solution in a large excess of hydrochloric acid, a heavy crystalline precipitate is formed, which, when recrystallised from a large quantity of boiling alcohol, yields long lemon-yellow needles consisting of dibromoparanitraniline (m. p. 202.5°).

The first of these reactions shows that the radicles Br and NO^2 stand to one another in the relation 1 : 3, while the second and third show that the NH^2 and NO^2 are in the position 1 : 4. Hence the formula above given (Körner).

(2). *Parabromorthonitraniline*, ($NH^2 : NO^2 : Br = 1 : 2 : 4$), is produced:—1. By heating nitro-*para*dibromobenzene, $C^6H_2Br_2NO^2.H.Br.H^2$, with concentrated alcoholic ammonia to 160° – 165° . The conversion is complete and unattended with formation of tarry products (Körner; Meyer a. Wurster). This base is also produced by nitration of parabromaniline (Hübner), and by heating the methylic ether of parabromortho-nitrophenol (2nd Suppl. 915) with alcoholic ammonia to 190° – 200° ; but the action is slow, a considerable proportion of the methylic ether remaining unaltered, even after heating for several days (Körner).

Parabromorthonitraniline forms orange-coloured felted needles melting at 111.4° , subliming without decomposition, and volatilising easily with vapour of water; dissolves readily in alcohol and ether, sparingly in cold water, more freely in hot water. It does not form salts, but dissolves easily in strong nitric and hydrochloric acids, and is separated from these solutions by water in its original state. It dissolves in dilute hydrochloric acid at the boiling heat, and crystallises out again on cooling. Its solution in hydrochloric acid stains a deal shaving yellow, quickly changing to red in contact with the air. The boiling aqueous solution dyes wool and silk a very fine yellow, which is not destroyed by soaping. By reduction with tin and hydrochloric acid, it yields a bromodiamidobenzene which is converted by sodium-amalgam into *orthodiamidobenzene*. With ethyl nitrite at ordinary temperatures it yields a diazo-amido-compound, which crystallises in large colourless rhombic plates, and when gently heated with a mixture of ethyl nitrite and alcohol, is converted, with evolution of nitrogen and formation of aldehyde, into *metanitrobromobenzene* (m. p. 56.4°). When finely pulverised, parabromorthonitraniline is suspended in dilute nitric acid, and air saturated with bromine-vapour is passed through it till an excess of bromine is present, dibromorthonitraniline (m. p. 127.3°) is produced, convertible by ethyl nitrite into symmetric nitrometadibromobenzene (m. p. 104.5°):—



(3). *Metabromorthonitraniline*, ($NH^2 : NO^2 : Br = 1 : 2 : 5$), is formed by heating nitrometadibromobenzene, $C^6H_2Br_2NO^2.H.H.Br.H$ (m.p. 61.6°), to 155° – 166° in sealed tubes for twelve to fifteen hours with alcoholic ammonia, and being but slightly soluble in alcohol, separates in the tubes on cooling, in prisms or needles. A further quantity may be separated from the solution in concentration and precipitation with

water. By recrystallisation from boiling alcohol it is obtained in large transparent reddish-yellow needles, having a faint blue reflex. It has a faint but agreeable odour; melts at 151.4° , and sublimes partially in small scales; is but very slightly soluble in water, even at the boiling heat; moderately soluble in hot, less soluble in cold alcohol.

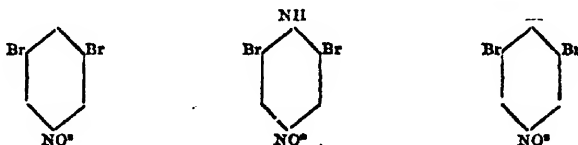
It dissolves with difficulty in acids. From solution in nitric acid of sp. gr. 1.38, it is precipitated in its original state by addition of water after a few hours; but after a longer time it undergoes transformation, and the solution then yields with potash a dinitro-metabromophenol, which crystallises in nearly colourless scales, melting at 81.4° .

This nitrobromaniline, reduced by tin and hydrochloric acid, yields a bromodi-amidobenzene convertible by sodium-amalgam into *orthodiamidobenzene*; treated with ethyl nitrite, it yields *paranitrobromobenzene*, which, after purification, melts at 125.5° . The bromine is, therefore, in the para-position with respect to the NO^2 , and this latter is in the ortho-position relatively to the NH^2 , as represented by the third structural formula on p. 199.

Dibromonitranilines, $\text{C}^6\text{H}^2\text{Br}^2(\text{NO}^2).\text{NH}^2$.

(1). *Diorthobromoparanitraniline*, ($\text{NH}^2 : \text{Br} : \text{NO}^2 : \text{Br} = 1 : 2 : 4 : 6$).—This base is formed: 1. By the action of bromine on hydrochloride of paranitraniline. 2. By passing bromine-vapour to saturation into hydrochloric acid in which orthobromoparanitraniline (p. 199) is suspended. 3. By heating nitrotribromobenzene (m. p. 111.9°) to about 150° in sealed tubes with alcoholic ammonia. 4. By treating the methylic ether of paranitro-dibromophenol, $\text{C}^6\text{OCH}^3.\text{H}.\text{Br}.\text{NO}^2.\text{Br}.\text{H}$, in the same manner.

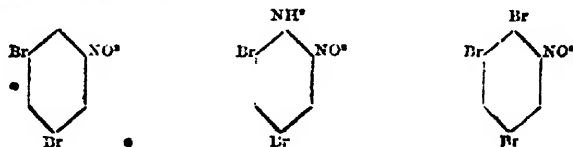
This base is nearly insoluble in water, and very slightly soluble in cold alcohol, but crystallises from a large quantity of boiling absolute alcohol in long thin light yellow needles, having a very faint blue reflex, and melting at 202.5° . It dissolves in nitric acid of sp. gr. 1.38, forming a nearly colourless solution, from which it is precipitated by water in its original state. Heated with strong potash-ley, it is converted into a red potassium salt [$\text{C}^6\text{H}^2\text{Br}^2(\text{NO}^2)\text{NK}^2$], from which it is reproduced by the action of water, or of dilute acids. By ethyl nitrite it is readily converted into *symmetric* nitro-dibromobenzene. By exchange of NH^2 for Br, by the diazo-reaction, it is converted into nitrotribromobenzene, $\text{C}^6\text{Br}.\text{br}.\text{H}.\text{NO}^2.\text{H}.\text{Br}$ (m. p. 111.9°). These reactions, together with its modes of formation, show that it has the constitution above indicated:—



(2). *Dibromorthonitraniline*, ($\text{NH}^2 : \text{NO}^2 : \text{Br} : \text{Br} = 1 : 2 : 4 : 6$), is formed: 1. By the action of bromine on the hydrochloride of orthonitraniline. 2. By the action of bromine on orthonitroparabromaniline. 3. By the action of alcoholic ammonia on dibromorthonitranisol, $\text{C}^6\text{OCH}^3.\text{NO}^2.\text{H}.\text{Br}.\text{H}.\text{Br}$. 4. By the action of the same reagent on nitrotribromobenzene, $\text{C}^6\text{Br}.\text{NO}^2.\text{H}.\text{Br}.\text{H}.\text{Br}$ (m. p. 119.5°). 5. By nitrating ordinary acetodibromanilide, and treating the resulting nitro-compound, $\text{C}^6.\text{NH}(\text{C}^6\text{H}^3\text{O}).\text{NO}^2.\text{H}.\text{Br}.\text{H}.\text{Br}$, with alcoholic ammonia.

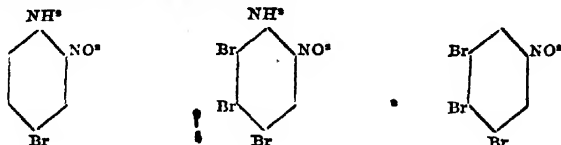
This base is considerably more soluble in alcohol than the para-compound last described, and crystallises therefrom on cooling, in stellate groups of transparent orange-coloured needles, which melt at 127.3° , and begin to sublime at the same temperature. It is but slightly soluble in cold water, somewhat more in hot water, moderately soluble in acids, e.g. in nitric acid of sp. gr. 1.38.

By ethyl nitrite, this base is easily converted into *symmetric* nitrometadibromobenzene (p. 177), and, by substitution of bromine for the residue NH^2 , into nitro-tribromobenzene melting at 119.5° :—

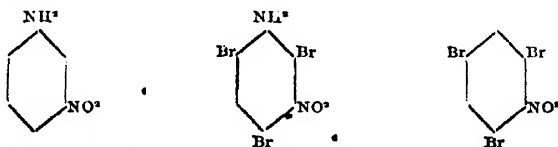


Tribromonitranilines, $\text{C}^6\text{HBr}^3(\text{NO}^2)\text{NH}^2$.

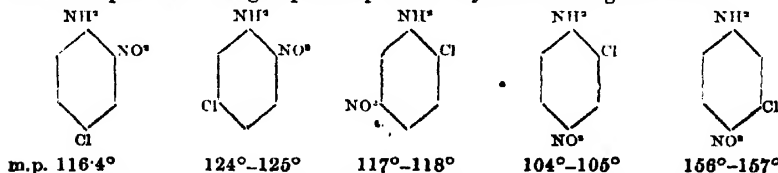
(1). *Tribromonitronitraniline*, ($\text{NH}^2 : \text{NO}^2 : \text{Br} : \text{Br} : \text{Br} = 1 : 2 : 4 : 5 : 6$), is produced by exposing (1 : 2 : 4), bromonitraniline (p. 200) suspended in hydrochloric acid to a current of air charged with bromine-vapour. It crystallises from alcohol in small lemon-yellow needles, melts at 161.4° , and is converted by ethyl nitrite into nitrotribromobenzene, $\text{C}^6\text{H}(\text{NO}^2)\text{Br}^3$, melting at 111.9° . This reaction and its mode of formation indicate its constitution:



(2). *Tribromometanitraniline*, ($\text{NH}^2 : \text{Br} : \text{NO}^2 : \text{Br} : \text{Br} = 1 : 2 : 3 : 4 : 6$), is formed by passing a current of air saturated with bromine-vapour through a dilute solution of metanitraniline in excess of hydrochloric acid, and separates at first in yellow-brown drops, which subsequently concrete into a light greenish-yellow crystalline precipitate. On washing this precipitate with water to remove hydrochloric and hydrobromic acids, then drying, and repeatedly crystallising from hot alcohol, it is obtained in transparent needles having a light greenish-yellow colour and strong vitreous lustre, and usually grouped in stars. It dissolves very easily in alcohol, and melts at 102.5° . Ethyl nitrite converts it into nitro- (1 : 3 : 5) bromobenzene (p. 181). This reaction, together with its formation from metanitraniline, indicates its constitution:—



Chloronitranilines, $\text{C}^6\text{H}^2\text{Cl}(\text{NO}^2)(\text{NH}^2)$, (Körner, *Gazzetta*, iv. 373; Bilsstein a. Kurbatow, *Deut. Chem. Ges. Ber.* ix. 633; *Liebigs Annalen*, clxxxii. 94). The known compounds of this group are represented by the following formulæ:—



(1). *Para-chloronitronitraniline*, ($\text{NH}^2 : \text{NO}^2 : \text{Cl} = 1 : 2 : 4$), is obtained by heating nitro-*para*-dichlorobenzene to 165° in sealed tubes with alcoholic ammonia, distilling off the greater part of the alcohol, precipitating and washing with water, and recrystallising from boiling water. It forms splendid needles sometimes flattened, having a deep orange-yellow colour, a peculiar odour, and melting at 116.4° (Körner); at 116° (B. and K.), that is to say, at a higher temperature than the corresponding bromonitraniline (p. 200). From alcohol, in which it is very soluble, it crystallises by spontaneous evaporation in spherical groups of needles of a still darker colour, approaching to brick-red. It is slightly volatile even at ordinary temperatures, and tinges paper yellow even at a considerable distance. With ethyl nitrite it yields (1 : 3) nitro-*chlorobenzene*; and by reduction, and prolonged treatment of the resulting bromo-diamidobenzene with sodium-amalgam, it is converted into (1 : 2) diamidobenzene. These reactions show that the radicals in this nitro-chloraniline are disposed in the manner above represented (Körner, *Gazzetta*, iv. 373).

(2). *Meta-chloronitronitraniline*, ($\text{NH}^2 : \text{NO}^2 : \text{Cl} = 1 : 2 : 5$), is obtained by heating *para*-nitro-*meta*-dichlorobenzene, $\text{C}^6\text{H}(\text{Cl})_2(\text{NO}^2)$ (p. 186), to 160° in sealed tubes for eight to twelve hours with alcoholic ammonia, partially distilling off the alcohol, precipitating with water, and recrystallising from hot alcohol (Körner). It may also be prepared from *m*-chloraniline, by first converting this base by means of acetyl chloride into *meta*-chloroacetanilide (crystals melting at 62.5°), and treating this compound with a mixture of nitric and sulphuric acid, whereby two nitro-derivatives are

formed, one of which, when decomposed by boiling with solution of sodium carbonate, yields a distillate containing metachlorororthonitraniline (Beilstein a. Kurbatow, *Deut. Chem. Ges. Ber.* ix. 634).

Metachlorororthonitraniline crystallises from alcohol in very thin yellow laminae several millimeters broad (Körner); from carbon sulphide, in which it is very slightly soluble, in yellow needles having a golden lustre (B. and K.). It melts at 123° , and begins to sublime at 112° (Körner); melts at 124° – 125° ; and its acetyl-derivative at 115° (B. and K.). It dissolves easily in strong nitric and hydrochloric acids, forming colourless solutions, from which it is precipitated unaltered by water. It is much more soluble in alcohol than the corresponding bromine-compound. By ethyl nitrite it is rapidly converted into parachloronitrobenzene. By reduction with tin and hydrochloric acid it yields monochlorororthodiamidobenzene, which, by the prolonged action of sodium-amalgam, is converted into orthodiamidobenzene (Körner).

(3). *Orthochlorometanitraniline*, ($\text{NH}^2 : \text{Cl} : \text{NO}^2 = 1 : 2 : 5$).—Prepared like the preceding compound, by nitration of orthochloraniline. Crystallises in easily soluble needles, melting at 117° – 118° . Its acetyl-derivative forms colourless needles, melting at 153° – 154° . The base, treated with alcohol and nitrous acid, is converted into p-chloronitrobenzene (Beilstein a. Kurbatow).

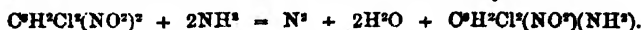
(4). *Orthochloroparanitraniline*, ($\text{NH}^2 : \text{Cl} : \text{NO}^2 = 1 : 3 : 4$).—Prepared by heating dichloronitrobenzene, $\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$ (m. p. 43°) with ammonia to 210° . Crystallises in light yellow needles, easily soluble in alcohol and carbon sulphide, melting at 104° – 105° . Its acetyl-derivative forms colourless needles melting at 189° . The base is converted by nitrous ether into metachloronitrobenzene.

(5). *Metachloroparanitraniline*, ($\text{NH}^2 : \text{Cl} : \text{NO}^2 = 1 : 3 : 4$).—Formed, together with m-chloro-o-nitraniline, by nitration of m-chloroacetanilide, &c. Crystallises from benzene in yellow laminae melting at 156° – 157° ; its acetyl-derivative melts at 141° – 142° . By treatment with nitrous ether the base is converted into orthochloronitrobenzene, melting at 32.5° and boiling at 243° (Beilstein a. Kurbatow).

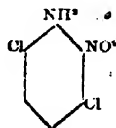
Chlorobromororthonitraniline, $\text{C}_6\text{H}_3\text{NH}_2\text{NO}_2\text{H.Cl.H.Br}$ (1 : 2 : 4 : 6).—This base is produced by passing air charged with bromine-vapour through moderately strong hydrochloric acid, in which finely pulverised parachlorororthonitraniline is suspended. As the point of saturation is attained, the volume of the liquid increases considerably, and the chloro-brominated base separates in the form of a microcrystalline chrome-yellow powder. After washing with water and recrystallisation from alcohol, it forms long shining transparent needles of a light orange-yellow colour, very much like the crystals of potassium picrate, and like the latter trichroic. It melts at 106.4° , and may be sublimed. Ethyl nitrite converts it into symmetric nitrochlorobromobenzene (p. 187) (Körner).

Dichloronitranilines, $\text{C}_6\text{H}_2\text{Cl}_2(\text{NO}^2)(\text{NH}^2)$.—Two modifications are known, one having its two chlorine-atoms in the para-, the other in the meta-position.

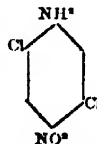
(1). *Paradichloronitraniline* is formed by heating β -dinitroparadichlorobenzene (p. 185) with alcoholic ammonia to 150° – 160° for several days:—



By concentrating the contents of the tube, precipitating, washing with water, and distilling with steam, it is obtained in yellow needles, melting at 66.4° , and easily subliming. By the action of ethyl nitrite it is converted into nitroparadichlorobenzene (m. p. 54.6°), which, when heated with alcoholic ammonia, yields parachlorororthonitraniline (m. p. 116.4°), and this by the action of ethyl nitrite is converted into metachloronitrobenzene (m. p. 48°). These transformations, as well as its formation from β -dinitroparadichlorobenzene, are consistent with either of the following formulæ:—



1 : 2 : 3 : 6.



1 : 3 : 4 : 6.

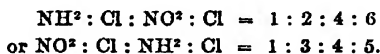
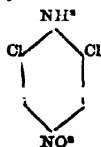
(Körner, *Gazzetta*, iv. 353).

(2). *Metadichloroparanitraniline*, $\text{C}_6\text{H}_3\text{NH}_2\text{Cl}_2\text{NO}_2\text{H.Cl}$.—O. N. Witt (*Deut. Chem. Ges. Ber.* vii. 1601) prepares this compound by adding acetodichloranilide (p. 6) to ice-cold nitric acid of sp. gr. 1.61, pouring the mixture immediately into ice cold

water, recrystallising the product from alcohol, and decomposing the resulting *aceto-nitrodichloranilide*, $C^6H^2Cl^2(NO^2).NH(C^2H^5O)$, (m. p. 188°), by quickly heating it with hydrochloric acid to 160° - 180° . The dichloronitraniline thus obtained crystallises from alcohol in tufts of orange-red needles melting at 100° . By treatment with nitrous ether it is converted into symmetric nitrodichlorobenzene ($NO^2 : Cl : Cl = 1 : 3 : 5$) melting at 64° - 65° .

Körner (*Gazzetta*, iv. 276) prepares the same dichloronitraniline by passing a very slow current of chlorine through a cooled solution of paranitraniline in a large excess of hydrochloric acid, and treating the resulting yellow precipitate—after washing with water and drying—with a large quantity of boiling alcohol, which leaves undissolved a quantity of metallicallly lustrous scales consisting of tetrachloroquinone, while the alcoholic solution on cooling deposits a crystalline magma of the dichloronitraniline, still mixed with a small quantity of tetrachloroquinone which cannot be separated by crystallisation. If, however, the dichloronitraniline, without further purification, be subjected to the action of nitrous ether, it is converted into symmetric nitrodichlorobenzene, which may be separated by distilling off the greater part of the alcohol, adding potash, and distilling in a current of steam, the tetrachloroquinone then remaining in the form of a potassium salt.

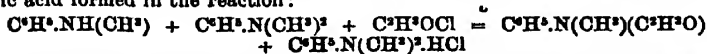
The formation of this dichloronitraniline by the processes above mentioned would not of itself be sufficient to determine the positions of the two chlorine-atoms; but its conversion into symmetric nitrodichlorobenzene by the action of nitrous ether shows that it must likewise have its two chlorine-atoms symmetrically situated with regard to the nitryl, and as it is moreover derived from paranitraniline, its constitution must be represented by the following formula:



Iodonitraniline. An iodonitraniline, probably having the structure $1 : 2 : 5$ or $C^6NH^2.NO^2.H.H.I.H$, is formed by heating nitrometadiodobenzene, $C^6.I.NO^2.H.H.I.H$, (m. p. 168.4°), with alcoholic ammonia to 170° for several days. It is purified by washing with water and recrystallisation from absolute alcohol, which latter operation must be performed in sealed tubes, inasmuch as the compound is but very sparingly soluble in alcohol boiling under ordinary pressure. It forms large lanceolate steel-blue laminae, which, when sufficiently thin, appear yellow by transmitted light. It does not melt at 220° , and is not attacked by ethyl nitrite (Körner, *Gazzetta*, iv. 386).

Alcoholic Derivatives of Aniline.

Methylanilines. Hofmann (*Deut. Chem. Ges. Ber.* vi. 338) finds that commercial methylaniline, boiling at 190° - 193° , is a mixture of monomethylaniline with aniline and dimethylaniline. The aniline is easily removed by adding dilute sulphuric acid as long as aniline sulphate separates out; and by treating the remaining liquid with an alkali, a mixture of mono- and di-methylaniline is obtained, which may be easily separated by treatment with acetyl chloride, whereby the monomethylaniline is converted into methylacetanilide, while the dimethylaniline combines with the hydrochloric acid formed in the reaction:



On pouring the product into hot water, the methylacetanilide separates on cooling in splendid long needles, and the mother-liquor, when concentrated, yields a further quantity of this compound, while dimethylaniline hydrochloride remains in solution. On distilling this liquid with an alkali, dimethylamine passes over first, and then more methylacetanilide. This last compound melts at 104° , and distils between 240° - 250° . It is slowly decomposed by alkalis, much more quickly by hydrochloric acid, yielding acetic acid and hydrochloride of methylaniline, from which the pure base may be obtained by distillation with an alkali.

Pure methylaniline has a sp. gr. of 0.976 at 15° , and boils at 190° - 191° . It does not give a violet colour with bleaching powder; neither does its oxalate yield aniline when heated.

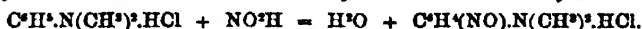
Dimethylaniline boils at 190°–191° (Hofmann). When it is heated to 160° for some hours with phosphorus trichloride, a large quantity of methyl chloride is given off, and the aqueous solution of the residue gives with caustic soda a precipitate containing much dimethylaniline; and on removing this by water, and crystallising the residue from alcohol, a white crystalline basic substance is obtained, apparently consisting of the phosphine base, $P[C^6H^4-N(CH^3)]^3$ (J. Hanimann, *Deut. Chem. Ges. Ber.* ix. 845).

Dimethylbromaniline, $C^6H^4Br.N(CH^3)^2$, is formed on adding bromine to a solution of dimethylaniline in acetic acid, and may be precipitated from the solution by addition of water or caustic soda. It crystallises from alcohol in silvery plates melting at 55°. Its hydrochloride is deliquescent, and yields a crystallisable platinum salt (Weber, *Deut. Chem. Ges. Ber.* viii. 714).

Nitromethylaniline, $C^6H^4.NH(CH^2NO^2)$, appears to be formed by the action of aniline on moist mercuric fulminate (p. 192).

Dimethylnitraniline, $C^6H^4(NO^2).N(CH^3)^2$, is obtained as a crystalline precipitate on adding strong nitric acid to a solution of dimethylaniline in 12 to 15 pts. of glacial acetic acid. It is slightly soluble in hot water, freely in alcohol, ether, and benzene, and crystallises in needles melting at 162°–163°; does not combine with hydrochloric acid (Weber).

Dimethylnitrosaniline, $C^6H^4(NO).N(CH^3)^2$.—The hydrochloride of this base is formed by the action of nitrous acid on the hydrochloride of dimethylaniline:



To prepare dimethylnitrosaniline, 100 pts. of amyl nitrite are added to a mixture of 50 pts. of dimethylaniline with 100 pts. of concentrated hydrochloric acid, and 750 pts. of a mixture of 1 vol. of hydrochloric acid with 2 vols. of alcohol which is well cooled with ice. After a short time, yellow needles separate; as soon as these no longer increase in quantity, the mass is thrown on a vacuum-filter and washed with ether-alcohol. An almost quantitative yield of pure dimethylnitrosaniline hydrochloride is thus obtained, in the form of small sulphur-yellow needles; these melt at 177°, but are apparently decomposed; they dissolve in water, forming an intensely yellow solution. On adding potassium carbonate to the hydrochloride suspended in water, the pure base separates in green flakes; it may be extracted with ether, and on evaporating the solution, is obtained in large green plates, which melt at 92°, and are slightly volatile in a current of steam. The sulphate and nitrate of the base are obtained in fine yellow needles on adding sulphuric or nitric acid to an ethereal solution of dimethylnitrosaniline. Dimethylnitrosaniline is easily reduced by tin and hydrochloric acid, a base different from dimethylaniline being produced. When boiled with an alkali, it is resolved into dimethylamine and nitrosophenol:



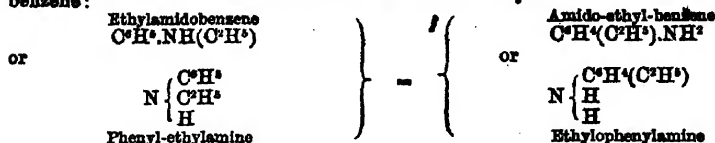
(Baeyer & Caro, *Deut. Chem. Ges. Ber.* vii. 809, 963).

Ethylaniline or Ethylamidobenzene, $C^6H^4.NH(C^2H^5)$, and Amido-ethylbenzene, $C^6H^4(C^2H^5).NH^2$ (A. W. Hofmann, *Deut. Chem. Ges. Ber.* vii. 526). Ethylaniline boils at 204°–205°, forms with platinum chloride an oily salt which gradually solidifies, and does not yield a crystalline salt with sulphuric acid or with aqueous hydrochloric acid; when, however, dry hydrochloric acid gas is passed into it, the liquid solidifies on cooling to a white crystalline mass.

Now when the ethylaniline hydrochloride thus obtained is heated in sealed tubes to 300°–330° for about three hours, it changes into a brown honey-like syrup, which does not exhibit any crystalline structure even after cooling; but if the heating be continued for twelve to eighteen hours, the syrup again changes to a mass of crystals imbedded in a brown resinous mother-liquor; and on treating this mass with water, which dissolves only the crystalline constituent, and mixing the filtered solution with alkali, a basic product is separated, the greater part of which distils between 212° and 216°, the thermometer, however, ultimately rising to 230°, showing that bases of higher boiling point are also present.

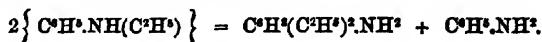
The base distilling between 212° and 216° yields a platinum salt having the same percentage composition as that of ethylaniline, but, unlike the latter, crystallising immediately in beautiful stellate groups of needles. Moreover, a drop of the base brought in contact with dilute sulphuric or hydrochloric acid immediately solidifies to a sparingly soluble crystalline mass. These characters, together with the higher boiling point, show that the base in question is not identical, but isomeric with ethylaniline. Further, this base, when repeatedly treated with methyl iodide, is converted into the iodide of a trimethylated ammonium base, $C^6H^4.NI = (C^6H^4.C^2H^5)(CH^3)^3NI$, showing that it is no longer a secondary but a primary amine. The ethylamido-

benzene has in fact been converted, by a shifting of the ethyl-group, into amide-ethyl-benzene:



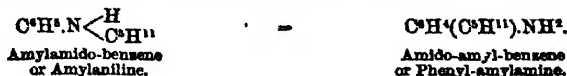
Amido-ethyl-benzene obtained as above is identical with the α -xylydine, boiling at 213° – 214° (Beilstein a. Kupfer), at 212° (Hofmann a. Martius), which is obtained by reduction of α -nitro-ethyl-benzene (1st Suppl. 292, 1181).

The higher-boiling portions of the basic products obtained by the action of heat on ethylaniline hydrochloride likewise consist mainly of amido-ethyl-benzene, mixed, however, with a small quantity of base having a diethylated phenyl-nucleus, whose formation may be represented by the equation:



Action of Nitrous Acid on Ethylaniline.—Griess formerly obtained by this reaction water, alcohol, and diazobenzene nitrate (iv. 430); but from recent experiments (Deut. Chem. Ges. Ber. vii. 218) he finds that the chief product is nitroso-ethyl-aniline, $\text{C}^6\text{H}_5\text{N} \begin{smallmatrix} \text{C}^2\text{H}_5 \\ \text{NO} \end{smallmatrix}$, which is easily obtained by passing a not too rapid current of nitrous acid into a solution of ethylaniline in dilute hydrochloric acid, or by mixing the solutions of ethylaniline hydrochloride and potassium nitrite. It is a heavy, yellowish oil, smelling like bitter almonds, and dissolving freely in alcohol and ether. It is perfectly neutral, and combines neither with bases nor with acids. On distilling it, the greater part is completely destroyed, and on dissolving it in strong hydrochloric acid or nitric acid, it is soon decomposed, with evolution of gas. On adding water to the solution in nitric acid, after it has stood for some hours, a compound is precipitated, which crystallises from alcohol in yellow needles. When an alcoholic solution of nitroso-ethyl-aniline is treated with zinc and sulphuric acid, it is re-converted into ethylaniline.

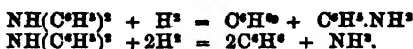
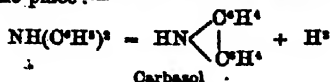
Amylaniline or Amylamidobenzene, $\text{C}^6\text{H}_5\text{.NH(C}^5\text{H}_{11}\text{)}$, and **Amido-amyl-benzene**, $\text{C}^6\text{H}_4\text{(C}^5\text{H}_{11}\text{).NH}^2$ (Hofmann, Deut. Chem. Ges. Ber. viii. 529). Amylaniline prepared by heating aniline hydrochloride with amylalcohol to 200° for twelve hours, and fractional distillation of the product, or by heating amyl iodide with aniline, boils at 258° , and exhibits the ordinary properties of secondary amines—that is to say, it does not solidify to a crystalline salt with either aqueous hydrochloric or sulphuric acid, and forms with platonic chloride an oily compound which slowly solidifies. When, however, it is saturated with dry hydrogen chloride, and the resulting hydrochloride is heated in sealed tubes to 300° – 340° for about twelve hours, a change takes place similar to that which is observed in the case of ethylaniline, a crystalline mass being formed, surrounded by a resinous substance; and on dissolving this crystalline product in water, and treating the filtered solution with an alkali, a basic oil is obtained, boiling at nearly the same temperature as amylaniline, but differing from that base in all its other properties, forming an easily fusible, but well-crystallised hydrochloride, a sparingly soluble, crystalline sulphate, and a well-crystallised platinohydrochloride having the same percentage composition as that of amylaniline. Moreover, when heated with methyl-iodide it takes up three methyl-groups, and is converted into the quaternary iodide, $(\text{C}^6\text{H}_4\text{.C}^5\text{H}_{11})(\text{CH}_3)_3\text{NI}$. These reactions show that the hydrochloride of amylaniline undergoes when heated a molecular transformation similar to that which takes place in ethylaniline, the amyl-group which in the amylaniline is directly united with the hydrogen, being transferred to the phenyl-group, and the secondary amine being thereby converted into a primary amine:—



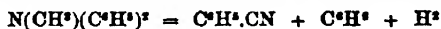
The molecular changes thus brought about by the action of heat on the hydrochlorides of ethyl- and amyraniline are exactly similar to those previously observed to take place in the methylanilines, whereby a quaternary compound was first converted into a ternary, this into a secondary, and the latter into a primary amine (2nd Suppl. 57).

Diphenylamine, $\text{NH}(\text{C}^6\text{H}_5)_2$. Commercial diphenylamine, after treatment with hydrochloric acid, and repeated crystallisation from hot ligroin, forms white shining plates resembling naphthalene, and melting at 54° (older statements give 46° as the melting point). It has a very faint odour when cold, becoming stronger on warming. Warm sulphuric acid dissolves it without coloration, but on raising the solution to a higher temperature, a deep blue tint is produced, ultimately changing to bluish green (Merz a. Weith, *Deut. Chem. Ges. Ber.* vi. 1611).

Decomposition by Heat.—When diphenylamine is passed through a red-hot tube, the following reactions take place :—



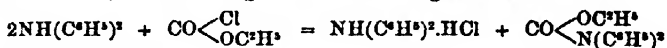
Methyldiphenylamine is decomposed at a much lower temperature than diphenylamine, but no methylcarbazol is formed. A great quantity of carbon separates out in the tube, and the volatile products consist of benzene, aniline, benzonitril, diphenylamine, carbazol, hydrogen, marsh-gas, and nitrogen. In this reaction, therefore, the methyl-group is first eliminated as marsh-gas, and the diphenylamine thus formed yields carbazol, aniline, and benzene. The formation of benzonitril is explained by the equation :



(Graebe, *Liebig's Annalen*, clxiv. 177).

Action of Carbonyl chloride on Diphenylamine.—When this gas (phosgene) is passed at 85° into a solution of diphenylamine in ligroin, the compound $\text{CO} \begin{array}{c} \text{Cl} \\ \text{N}(\text{C}^6\text{H}_5)_2 \end{array}$ is produced, which, when treated with ammonia, aniline, or diphenylamine, is converted into a phenylated carbamide (Michelet, *Deut. Chem. Ges. Ber.* viii. 1664).

Action of Ethyl-chlorocarbonate.—When solutions of this ether and diphenylamine in benzene are mixed and gently heated, diphenylamine hydrochloride is deposited, and the filtrate leaves on evaporation a crystalline mass, which, after crystallisation from amyl-alcohol, yields diphenylurethane, $\text{CO} \begin{array}{c} \text{OC}^6\text{H}_5 \\ \text{N}(\text{C}^6\text{H}_5)_2 \end{array}$, in slender colourless prisms melting at 66° – 72° , and remaining unaltered when digested with aniline :



(Merz a. Weith, *loc. cit.*)

Action of Oxalic Acid.—When diphenylamine is heated with oxalic and hydrochloric acid, formodiphenylamine, $(\text{C}^6\text{H}_5)_2\text{N}\cdot\text{COH}$, is produced, together with a blue colouring matter which appears to contain the hydrochloride of a complex amine, formed from several diphenylamine-residues united by a carbon-atom, or by the group CH or CH^2 (Girard a. Willm, *Bull. Soc. Chim.* [2], xxiv. 99).

Diphenylamine-sulphonic acids.—When 6 pts. of strong sulphuric acid are digested with 5 pts. of diphenylamine, and the product is treated with hot water, a considerable quantity of unaltered diphenylamine remains undissolved, and the liquid

alcohol, easily soluble nodular crystals, consisting of *barium diphenylaminedisulphonate*, $\text{C}^{12}\text{H}^{10}\text{N}(\text{SO}_3)_2\text{Ba}$. *Diphenylamine-monosulphonic acid* is obtained by decomposing its barium salt with sulphuric acid. It forms a crystalline mass consisting of white leaflets, which become blue on exposure to the air, and melt, with decomposition, at 200° , yielding diphenylamine and sulphuric acid. The *potassium salt*, $\text{C}^{12}\text{H}^{10}\text{NSO}_3\text{K}$, forms white shining leaflets easily soluble in water and slightly soluble in alcohol. The *lead salt*, $(\text{C}^{12}\text{H}^{10}\text{NSO}_3)_2\text{Pb}$, forms tufty or nodular crystals slightly soluble in water.

The sulpho-acids of diphenylamine give a deep violet colour with potassium chlorate, and a solution of either of these sulpho-acids in hydrochloric acid gives a green colour with potassium permanganate, green flakes being finally deposited. Moreover, a tint similar to that of iodine dissolved in carbon sulphide is produced by heating either of these sulpho-acids with oil of vitrol.

When diphenylamine is heated to 206° with sulphuric acid, sulphur dioxide is

evolved, and the product contains, not only the sulpho-acids already described, but also a brown substance insoluble in water, soluble in alkalis, and precipitated by acids (Merz a. Weith).

The diphenylamine-sulphonic acids heated to 200° with small quantities of hydrochloric acid are resolved into sulphuric acid and diphenylamine (Girard, *Bull. Soc. Chim.* [2], xxiii. 2).

Alcoholic Derivatives of Diphenylamine are obtained by the action of diphenylamine and hydrochloric acid, in varying proportions, on different alcohols. Methyl-diphenylamine boils at 282°, ethyldiphenylamine at 295°–297°, amyldiphenylamine at 330°–340°. These substances, heated with oxalic acid, or with oxalic and sulphuric acid, are converted into blue colouring matters (Girard, *Bull. Soc. Chim.* [2], xxiii. 2).

Derivatives of Diphenylamine containing Acid Radicles.—Formodiphenylamine, $(C^6H^5)_2N.CO.H$, is produced, with elimination of water, by the action of formic acid on diphenylamine, and occurs, as already mentioned, amongst the products of the action of oxalic acid on diphenylamine (p. 207). It is insoluble in water, but soluble in benzene and in alcohol, crystallising from the latter, by spontaneous evaporation, in large orthorhombic crystals. Treated with sulphuric acid it evolves pure carbonic oxide; the action both of reducing and of oxidising agents reproduces diphenylamine. A solution of potassium hydrate, or water alone at 140°, causes it to split up into formic acid and diphenylamine (Girard a. Willm).

Acetyldiphenylamine, $N(C^6H^5O)(C^6H^5)^2$.—When acetyl chloride is added to a solution of diphenylamine in benzene, a crystalline precipitate is formed, which increases in quantity on the application of heat; and the filtrate yields on evaporation a crystalline residue of acetyldiphenylamine, which, after repeated crystallisation from ligroin, is obtained in colourless plates, melting at 95° (Merz).

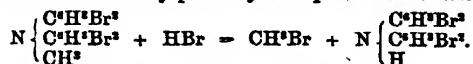
Bromodiphenylamine (R. Gnehm, *Deut. Chem. Ges. Ber.* viii. 925).—Hofmann, by treating an alcoholic solution of diphenylamine with bromine, obtained tetrabromodiphenylamine, $NH(C^6H^4Br)^2$, as a yellowish precipitate easily soluble in alcohol and crystallising therefrom in beautiful needles (iv. 453). According to Gnehm, this compound crystallises in colourless transparent needles or prisms, insoluble in water, only slightly soluble even in hot alcohol, easily soluble in benzene, and melting at 182°. Heated with acetyl chloride, it yields acetotetrabromodiphenylamine, melting at 158°.

Hexbromodiphenylamine, $NH(C^6H^4Br)^3$, is obtained, together with tetrabromodiphenylamine, on adding bromine to a solution of diphenylamine in acetic acid. It melts at 218°, is insoluble in water, almost insoluble in alcohol, and moderately soluble in benzene, from which it separates in colourless prismatic crystals.

Sodium-amalgam removes the bromine from these compounds, converting them into diphenylamines.

Bromomethyldiphenylamines.—When bromine is added to a solution of methyl-diphenylamine in acetic acid, the mixture becomes hot, evolves hydrobromic acid, and finally solidifies to a crystalline mass. Fractional crystallisation separates this product into three portions, the least soluble being *tribromomethyldiphenylamine*, $N \begin{Bmatrix} C^6H^5Br \\ C^6H^5Br \\ OH \end{Bmatrix}$, which forms colourless needles melting at 98°, and dissolving readily in benzene.

The fraction having an intermediate solubility in alcohol consists of *tetrabromomethyldiphenylamine*, $N \begin{Bmatrix} C^6H^5Br \\ C^6H^5Br \\ CH^3 \end{Bmatrix}$, which forms needles and prisms melting at 129°, and dissolving readily in benzene. The third or least soluble fraction is *tetrabromodiphenylamine*, and its formation may probably be represented as follows:—



The methyl may be removed from either of the above-described methylated bromodiphenylamines by digestion with *glacial acetic acid* and *bromine*, either tetrabromodiphenylamine or hexbromodiphenylamine being formed.

Sodium-amalgam removes the bromine, leaving methyldiphenylamine.

Tribromomethyldiphenylamine is readily attacked by hot nitric acid, a resinous product being formed, and the continued action of fuming nitric acid on this compound leads to the formation of *tetranitrodibromodiphenylamine*, which separates from glacial acetic acid in beautiful yellow leaflets, melting and decomposing at 235°–242°, and dissolving readily in alkalis.

The other brominated bodies above described yield small proportions of nitro-compounds, perhaps identical with that just described.

Chlorodiphenylamines.—A solution of diphenylamine in glacial acetic acid absorbs dry chlorine, giving off hydrochloric acid, and after a time deposits crystals consisting chiefly of *tetrachlorodiphenylamine*, $\text{NH}(\text{C}^6\text{H}^4\text{Cl})_2$. This body, when pure, forms colourless prisms, melting at $133^\circ\text{--}134^\circ$, and dissolving easily in alcohol, benzene, ether, carbon bisulphide, and chloroform.

An acetic acid solution of methyl-diphenylamine likewise absorbs dry chlorine, with evolution of much heat, and yields products which differ according to the strength of the solution, and other conditions. One of these forms colourless prisms, melting at $96^\circ\text{--}97^\circ$, and easily soluble in the same liquids as the foregoing compound. This is probably *tetrachloromethyl-diphenylamine*, $\text{NCH}_2(\text{C}^6\text{H}^4\text{Cl})_2$, but the presence of methyl in it has not been actually demonstrated.

The crude product of the action of chlorine on methyl-diphenylamine, when treated with nitric acid, yields tetrachloroquinone (chloranil).

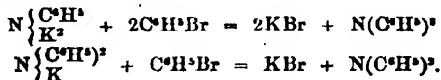
Methyl-diphenylamine, heated to 150° with fuming hydrochloric acid, in a sealed tube, is resolved into methyl chloride and diphenylamine (Gnehm, *Deut. Chem. Ges. Ber.* viii. 1040).

Diphenylnitrosamine, $\text{N}(\text{C}^6\text{H}_5)_2\text{NO}$, is obtained as a crystalline precipitate by acting with 15 pts. of crude ethyl nitrite on one part of diphenylamine, at a temperature below 0° . After being washed with ice-cold alcohol, it is dissolved in an equal weight of warm benzene, and the cold solution mixed with an equal volume of alcohol, and left to evaporate.

The same compound is very readily formed by adding diphenylamine hydrochloride to a solution of an equal weight of potassium nitrite acidulated with acetic acid; also by dissolving 2 pts. of diphenylamine in 4 pts. of benzene, and adding 3 pts. of pure ethyl nitrite.

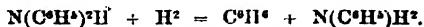
Diphenylnitrosamine crystallises in brilliant, pale-yellow, four-sided plates, melting at 66.5° , and dissolving readily in cold acetic acid and aldehyde, in hot alcohol and benzene, sparingly in hot petroleum, but not in petroleum-naphtha. It is not acted on by water, dilute acids, or alkalis, and dissolves in sulphuric acid with a beautiful blue colour, like diphenylamine. When sodium-amalgam is added to its alcoholic solution, ammonia is evolved; and by treatment with tin and hydrochloric acid it is converted into a resin consisting chiefly of diphenylamine (O. N. Witt, *Deut. Chem. Ges. Ber.* viii. 855).

Triphenylamine, $\text{N}(\text{C}^6\text{H}_5)_3$ (Merz a. Weith, *Deut. Chem. Ges. Ber.* vi. 1154). This base is produced by the action of bromobenzene on dipotassium-aniline, or on potassium-diphenylamine:



Potassium dissolves in aniline, eliminating hydrogen, together with a trace of ammonia, and when the product thus obtained is digested with bromobenzene, a very violent reaction takes place. The whole being now treated with dilute hydrochloric acid, to remove aniline and bromobenzene, an oily substance remains, and this when fractionated, first yields diphenylamine, which passes over at about 300° , and then a thick oil, which distils at a much higher temperature, and solidifies on cooling to a crystalline mass, which, when crystallised from alcohol, exhibits the composition of triphenylamine. These results show that *potassium-aniline* and *dipotassium-aniline* are both formed during the action of potassium on aniline.

When melted diphenylamine is treated with potassium, hydrogen is evolved, and a small portion of aniline is formed by the reducing action of this hydrogen on the diphenylamine—



Potassium-diphenylamine must, however, be formed at the same time, as the product, when treated with bromobenzene, yields triphenylamine. In preparing triphenylamine from diphenylamine, it is advantageous to dissolve the diphenylamine in aniline before treating it with potassium; the product may be easily freed from diphenylamine by crystallisation from alcohol.

Triphenylamine melts at 127° ; it is very slightly soluble in cold alcohol, slightly soluble in hot alcohol, and moderately soluble in benzene. It separates from alcohol in small scales, from ligroin in large crystals, and from ether in shining pyramids. It does not exhibit basic properties, not combining even with picric acid. *Acetyl*

chloride does not attack it when added to its solution, in benzene, but when heated with it to 100°, yields a greenish flocculent substance, which is probably an addition-product. Triphenylamine dissolves in cold sulphuric acid, giving a violet colour, which changes to blue; but if the mixture be allowed to stand for some time, or if heat be applied, the colour disappears.

A solution of triphenylamine in acetic acid is coloured green by the addition of nitric acid, but if more nitric acid is added, the liquid becomes yellow and deposits yellow flocks.

Diamidobenzene or Phenylene-diamine, $C_6H_4(NH_2)_2$. *Occurrence of the Meta-modification as a By-product of the Manufacture of Aniline.*—An aniline-oil from Weiler's aniline manufactory at Köln, nine-tenths of which distilled between 270° and 300°, was found to consist in great part of phenylene-diamine.

The purification of this body may be effected by adding crude hydrochloric acid to the oil, and dissolving the mass of crystals thus formed in the smallest possible quantity of boiling water; this solution is filtered hot to remove resinous bodies, and left to crystallise, then recrystallised with animal charcoal. The crystals, after washing with concentrated hydrochloric acid, consist of pure phenylene-diamine hydrochloride.

The phenylene-diamine is doubtless formed from the dinitrobenzene contained in the nitrobenzene used for the preparation of the aniline, and must therefore be *α*- or *meta*phenylene-diamine, $C_6H_4.NH_2.H.NH_2.H^+$ (Hofmann, *Deut. Chem. Ges. Ber.* vii. 812).

Diacetometaphenylene-diamine, $C_6H_4(NH.COCH_3)_2$, is formed by heating the diphenylene-diamine just described with 2½ mols. glacial acetic acid till the mass becomes solid on cooling; by solution in hot water and cooling, it is obtained in crystals which melt at 191°, and are slightly soluble in cold water, but dissolve more readily in hot water and in alcohol (Barbaglia, *Deut. Chem. Ges. Ber.* vii. 1257).

*Nitrodiacono-*m*-phenylene-diamine, $C_6H_3(NO_2)(NH.COCH_3)_2$,* is formed when a solution of diaceto-*m*-phenylene-diamine in glacial acetic acid is gradually added to fuming nitric acid. It crystallises from alcohol in groups of short slender needles, moderately soluble in alcohol, ether, and glacial acetic acid, and melting at 246°. By the action of boiling caustic soda it is converted into a nitrophenylene-diamine, $C_6H_3(NO_2)(NH_2)_2$, soluble in water, more soluble in alcohol and ether, melting at 161°, and isomeric with the nitrophenylene-diamine (so-called *azophenylamine*) which Gottlieb obtained by treating dinitraniline with ammonium sulphide (iv. 481).

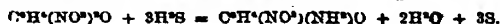
If the action of the caustic soda be further prolonged (to ten or fifteen hours) the nitrophenylene-diamine is converted into a nitramidophenol, $C_6H_3(NO_2)(NH_2)OH$, melting at 133°–134°, and isomeric with that which Laurent a. Gerhardt obtained by reduction of ammonium dinitrophenate (iv. 398).*, By still further prolonging the action of the caustic soda, nitrometadioxybenzene, or nitroresorcin, $CH_3(NO_2)(OH)_2$, appears to be formed, but this result has not been distinctly proved. According to Wagner, indeed, the replacement of amidogen by hydroxyl in nitro-compounds under the influence of alkalis is practicable only when amidogen-groups are present previous to nitration; thus dinitrobenzene furnishes a nitraniline which will not thus decompose, whereas the nitraniline from acetanilide readily exchanges NH_2 for OH (Barbaglia).

Paradiamidobenzene, or β -Phenylene-diamine, $C_6H_4.NH_2.H.H.NH_2.H^+$.—Biedermann a. Ledoux (*Deut. Chem. Ges. Ber.* vii. 1531) have obtained this compound by reduction of nitraniline (from acetanilide) with tin and hydrochloric acid. The free base is most conveniently isolated by dry distillation of the hydrochloride with sodium carbonate. It is thus obtained quite pure, and melting at 147°.

*Diaceto-*p*-phenylene-diamine, $C_6H_4(NH.CO.CH_3)_2$,* obtained by boiling this base with glacial acetic acid, crystallises in small, hard, very sharply defined quadratic octohedrons, which melt at a temperature above 295°, and dissolve but sparingly in all the ordinary solvents except glacial acetic acid, which dissolves them more freely. Their solution in excess of glacial acetic acid, treated with fuming nitric acid, yields, as chief product, *dinitrodiacono-*p*-phenylene-diamine*, a body melting at 258°, sparingly soluble in alcohol and acetic acid.

*Dinitro-*p*-phenylene-diamine, $C_6H_3(NO_2)_2(NH_2)_2$,* is obtained by heating the last-mentioned compound with alcoholic ammonia in sealed tubes to 150°. It crystallises in fine red needles melting at 294°, soluble in hot water and in alcohol, slightly soluble in ether. The salts contain only 1 mol. of acid to 1 mol. of the nitro-base.

* The formula there given for the nitro-amidophenyl (nitrophenamido acid) and the equation representing its formation, are erroneous: the equation should be:—



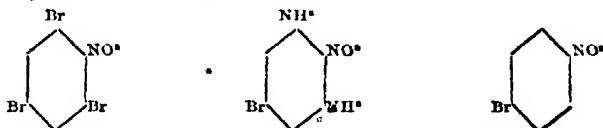
A dichlorophenylene-diamine, either $\text{C}^6\text{H}_3\text{Cl}_2\text{NH}_2\text{Cl.H}^+$, or $\text{C}^6\text{H}_3\text{Cl}_2\text{NH}_2\text{Cl.H}^+$, crystallising from alcohol in long flexible needles having a satiny lustre and melting at 60° , is obtained by the action of tin and hydrochloric acid on the dichloronitraniline, which melts at 100° (p. 203). (O. N. Witt, *Deut. Chem. Ges. Ber.* vii. 1604).

On boiling it with soda-ley, in which it is likewise soluble, ammonia is given off, the liquid assumes a dark red colour, and a yellow indistinctly crystalline body is formed, which dissolves very easily in water and in alcohol, and appears, from the analysis of its barium and silver salts, to be a dinitrodioxybenzene. Its formation is in accordance with Wagner's view above-mentioned.

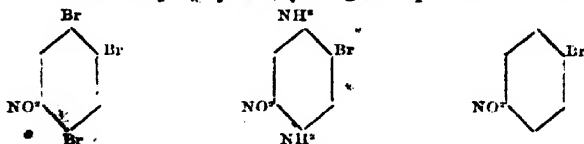
Mononitraceto-p-phenylene-diamine, $\text{C}^6\text{H}_3(\text{NO}_2)(\text{NH.CO.CH}_3)_2$, obtained by the action of fuming nitric acid on a well-cooled solution of diacetophenylene-diamine in a large quantity of glacial acetic acid, crystallises in golden yellow needles having a silky lustre, and melting at 184° .

Mononitro-p-phenylene-diamine, $\text{C}^6\text{H}_3(\text{NO}_2)(\text{NH}_2)_2$, obtained by gently heating this last compound with soda-ley, crystallises in dark red needles, melts at 195° , dissolves in water and in alcohol, is insoluble in alkalis at ordinary temperatures, but gives off ammonia when boiled with them; forms mono-acid salts. It is identical with the nitrophenylene-diamine which Gottlieb obtained by the action of ammonium sulphide on dinitraniline (iv. 482).

NITROBROMOPHENYLENE-DIAMINES, $\text{C}^6\text{H}_3(\text{NO}_2)\text{Br}(\text{NH}_2)_2$ (Körner, *Gazzetta*, iv. 414, 423).—(1). *Paranitrobromometaphenylene-diamine*, $\text{C}^6\text{H}_3\text{Br}(\text{NO}_2)(\text{NH}_2)_2$, (1 : 2 : 3 : 5), is produced by heating nitro- (1, 3, 5) tribromobenzene to 170° – 180° in sealed tubes for several days with alcoholic ammonia. The resulting red-brown solution, as soon as it ceases to deposit crystals on cooling, is taken out of the tubes and evaporated; the residue, after washing with water, to remove ammonium bromide, is crystallised from a large quantity of boiling alcohol. The base is thus obtained in splendid orange-red needles which acquire a golden lustre on drying. For perfect purification, however, it must be once recrystallised from water, the crystals being collected while the solution is still tepid; otherwise they will be accompanied by a small quantity of a lighter-coloured compound containing water of crystallisation. The base does not melt at 150° , but begins to soften at 163° , and then sublimes partially in ruby-red needles, the greater part, however, turning brown and decomposing. Heated with a large excess of ethyl-nitrite, it is converted into *para*-nitrobromobenzene. This reaction and the formation of the base from nitrotribromobenzene (NO_2 , 1 : 3 : 5), establish its constitution:—



(2). *Paranitrobromoparaphenylene-diamine*, $\text{C}^6\text{H}_3\text{Br}(\text{NO}_2)(\text{NH}_2)_2$, (1 : 2 : 4 : 5), is formed by heating the corresponding nitrotribromobenzene (m. p. 93.5°) to 100° – 120° , in sealed tubes for about twelve hours, with excess of alcoholic ammonia. An orange-coloured solution is thus formed, containing splendid needles and prisms, which may be freed from ammonium bromide by washing with moderately strong alcohol. By recrystallisation from boiling alcohol, in which it is slightly soluble, the base may be obtained in pyramidal needles resembling slowly crystallised potassium picrate, and, like the latter, exhibiting trichroism. By heating with alcohol in sealed tubes to 150° , and slow cooling, it is obtained in larger prisms having a fine orange colour. It melts at 166° , and is not altered by heating with aqueous potash. Gently heated with a solution of nitrous acid in absolute alcohol, it dissolves slowly, with evolution of nitrogen and aldehyde, and the solution on cooling yields paranitrobromobenzene in needle-shaped crystals, melting after purification at 125.5° :—



Violet Dye obtained by the Action of Sulphur on Paraphenylene-diamine.—When this base is heated to 150° – 180° with its own weight of sulphur, a large quantity of hydrogen sulphide is evolved; and on dissolving the residue in hot water, filtering,

and treating the filtrate with oxidising agents, splendid violet and blue colours are obtained. The sulphuration and oxidation may perhaps be most advantageously effected in one process. For this purpose the hydrochloric acid solution of the phenylene-diamine is saturated with hydrogen sulphide, and mixed with ferric chloride. The sulphur thereby set free combines in the nascent state with the base, and on gradually adding the oxidising agent, the colouring matter will develop itself and be precipitated. After filtration, the impurities are removed by washing with water, and dissolving the residue in hot water; if the liquid is then left to cool, a pure and magnificently crystallised product is obtained. For 20 grams of the phenylene-diamine hydrochloride the following quantities of material are used:—

Sulphuretted hydrogen water	4000 c.c.
Hydrochloric acid	20 grams.
Ferric chloride (1 in 10 solution)	500 c.c.

This violet colour surpasses in brilliancy the *violets de Paris*. In its dry state it has a dark greenish-brown colour, and readily crystallises in long silky fibres. It is very soluble in pure water, but the smallest quantity of foreign matter modifies its solubility. If soda be added to the violet solution, a brown precipitate is obtained, which forms the base of the new colour. Acids precipitate the solution, but an excess of acid redissolves the precipitate. Acetic acid forms a violet, mineral acids a pure blue solution. Metallic salts give a violet precipitate, which redissolves when the salt has been eliminated by washing. Zinc chloride gives a very bulky violet precipitate; sodium chloride separates the violet from its solution, but transforms it partly into a new violet substance, insoluble in water. If this precipitation be repeated several times, a complete transformation ensues, the soluble colouring matter disappearing entirely. Tannin forms, with the violet, a compound insoluble in water. Reducing agents decolorise it, but mere agitation in contact with air will reproduce the primitive colour. Oxidising agents destroy the colour very rapidly.

The violet dye is capable of giving by substitution other colouring derivatives; if heated with aniline, it gives a blue insoluble in water and soluble in alcohol if submitted to the action of aldehyde, methyl iodide, &c.; under ordinary conditions, it is transformed into a pure bluish-green. The part played by the sulphur in its formation has not yet been made out (C. H. Lauth, *Compt. rend.* lxxiii. 1441).

Azobenzene, $\text{C}_6\text{H}_5\text{—N=N—C}_6\text{H}_5$.—According to Anschütz a. Schultz (*Deut. Chem. Ges. Ber.* ix. 1398), this compound is the chief product formed by the action of sodium on parabromaniline. The statement of Glaser (*Zeitschr. f. Chem.* 1866, 310) that benzidine is formed by this reaction appears to be incorrect.

By the action of antimony trichloride, azobenzene is converted into a black amorphous substance having a conchoidal fracture and metallic lustre, soluble with dark red colour in water, and more easily in alcohol; it probably contains a compound analogous to rosaniline or violaniline (Bogdanoff, *Ber.* ix. 1598).

Nitromethyl-azobenzene, $\text{C}_6\text{H}_5\text{.N}^+\text{.CH}_2(\text{NO}^-)$, is formed by mixing the aqueous solution of sodium-nitromethane with the equivalent quantity of diazobenzene nitrate. It crystallises from alcohol in slender cherry-red needles, from carbon sulphide in prisms; melts with decomposition at 153° , and detonates at a higher temperature. It dissolves in strong sulphuric acid with a deep blue-violet colour. Fuming hydrochloric acid at the boiling heat converts it into a white substance (Fries, *Ber.* viii. 1078).

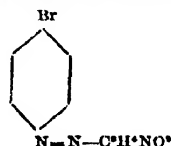
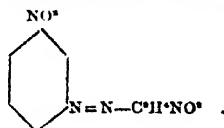
Nitroethyl-azobenzene, $\text{C}_6\text{H}_5\text{.N}^+\text{.C}_2\text{H}_4\text{NO}^-$, is prepared by mixing the solutions of diazobenzene sulphate and sodium-nitroethane, or more advantageously by treating a very dilute solution of aniline nitrate with potassium nitrite, and adding the mixed solution to an alkaline solution of nitroethane. It forms orange-coloured rectangular crystals, melting with decomposition at $136^\circ\text{--}137^\circ$, easily soluble in alcohol and ether, insoluble in cold water, dissolving with blood-red colour in alkalis, and precipitated therefrom by acids. Strong sulphuric acid dissolves it with violet-red colour, soon becoming dingy. Its ammoniacal solution is precipitated by metallic salts, and the compound itself is reduced to a colourless body by tin and hydrochloric acid. It dyes silk a pure and deep yellow, and forms salts containing 2 atoms of univalent metal (V. Meyer a. G. Ambühl, *Deut. Chem. Ges. Ber.* viii. 751, 1073).

When a solution of nitroethyl-azobenzene in a slight excess of ammonia is left to evaporate, it solidifies after a short time to a pulp of orange-coloured stiffening lamine, consisting, not of an ammonium-salt, but of the free azo-compound, which appears, therefore, to be incapable of fixing ammonia in the solid state. The same is the case with the other mixed azo-compounds (Barbieri, *Deut. Chem. Ges. Ber.* ix. 389).

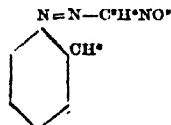
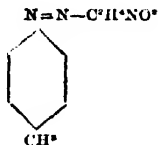
Nitroethyl-metazonitrobenzene, $C^6H^4NO^2.N^2.C^2H^4NO^2$, is precipitated on adding potassium-nitroethane to a solution of diazobenzene nitrate, and forms, after purification, a yellow powder easily soluble in hot alcohol, and dissolving with red colour in alkalis. Its sodium salt is sparingly soluble in water, and is thrown down from the red solution of the potassium salt by soda-ley in the form of an orange-coloured precipitate. Its solution gives coloured precipitates with metallic salts, dark-red brown with silver nitrate, yellow with lead acetate, greenish-yellow with cupric sulphate. The azo-compound, treated with tin and hydrochloric acid, yields a base, the stannochloride of which has the composition $C^6H^{10}N^4Cl^2.SnCl^4$. The free base and its hydrochloride are very unstable (F. Hallmann, *Deut. Chem. Ges. Ber.* ix. 389).

Nitroethyl-parazobromobenzene, $C^6H^4(Br.N^2.C^2H^4NO^2)$.—The potassium salt of this compound separates as a bulky brown-red crystalline precipitate, on adding potassium nitroethane to a solution (even very dilute) of the diazo-salt produced by the action of potassium nitrite on parabromaniline dissolved in 2 mols. nitric acid; and on adding dilute sulphuric acid to the solution of this salt, the azo-compound separates as a yellow precipitate, which may be purified by washing with water and crystallisation from hot dilute alcohol. It forms small, shining, brick-red crystals, soluble in ether, glacial acetic acid, chloroform, &c.; melts, with decomposition, at 135° – 138° , when quickly heated; by prolonged heating it is decomposed even below 100° . Strong sulphuric acid dissolves it with deep violet, but transient colour. The solution of the potassium salt gives with silver nitrate a deep orange-coloured precipitate, which soon turns black, with lead acetate a light yellow, and with cupric sulphate a greenish-yellow precipitate (H. Wald, *Deut. Chem. Ges. Ber.* ix. 393).

The last two compounds may be represented by the following structural formulæ:



Nitroethyl-azomethylbenzene, or *Nitroethyl-azotoluene*, $C^6H^4(CH^3).N^2.C^2H^4NO^2$.—This compound is known in two modifications, *para* and *ortho*:



The *para*-compound is precipitated as a potassium salt on adding potassium-nitroethane to the aqueous solution of the diazo-salt prepared by the action of nitrous acid on a salt of paratoluidine, and may be isolated and purified (by crystallisation from hot alcohol) in the same manner as nitroethyl-azobenzene. It forms splendid orange-red prisms, having a characteristic steel lustre, and exhibits a close resemblance to the isomeric compound, nitroethyl-azobenzene (p. 214), and to nitroethyl-azobenzene; melts, with evolution of gas, at 133° . When suspended in strong sulphuric acid, it dissolves to a splendid fuchsine-red liquid, the colour of which, like that of the corresponding benzene-compound, quickly becomes dingy. It resembles the benzene-compound in being somewhat unstable; a well-crystallised preparation which had remained unaltered for several months, suddenly decomposed and was converted into a dark-coloured resinous mass. It dissolves in alkalis with deep red colour, forming salts very much like those of the preceding compounds. The aqueous solution of the sodium salt gives a yellow precipitate with mercurous nitrate; dark yellow with mercuric chloride; red-brown, quickly blackening, with silver nitrate; yellowish-red with lead acetate; yellow with cupric sulphate and with zinc chloride.

Nitroethyl-azo-orthotoluene is prepared in like manner from orthotoluidine. It differs from all the preceding compounds in its great tendency to become resinous when separated from the not quite pure solution of the potassium salt. Before adding the potassium-nitroethane, it is necessary to free the solution of the diazo-salt, by filtration, from a gummy substance which separates from it. The *neutral sodium salt*, $C^6H^4N^2O^2Na$, is precipitated by soda-ley, even from very dilute solutions of the potassium salt, in spangles having a brilliant golden lustre.

The azonitro-compound is separated by dilute sulphuric acid from the solution of its salts as a yellow precipitate which, when recrystallised from alcohol, forms broad orange-coloured needles melting at 87° – 88° . It dissolves in strong sulphuric acid, with a fine red colour which disappears after a short time. The precipitates which it forms with metallic salts resemble those of the para-compound, excepting that the red flocks of the silver salt have a finer and more fiery tint. Both these toluene-compounds dye silk like the benzene-compound (Barbieri, *Deut. Chem. Ges. Ber.* ix. 386).

Nitropropyl-azobenzene, $C^6H^5.N^2.O^2H = C^6H^5.N^2.C^3H^5.NO^2 = N-C^6H^5$

$N-CH(NO^2)-CH^2-CH^3$.—This compound, formed by the action of primary nitropropane on diazobenzene nitrate, crystallises in dark orange-coloured needles, melting at 98° – 99° , easily soluble in hot alcohol, dissolving with deep red colour in alkalis. Like the homologous ethane- and methane-compounds, which it otherwise resembles, it is an acid body, and is thereby distinguished from the isomeric isopropyl-compound, which is neutral (V. Meyer, *Deut. Chem. Ges. Ber.* ix. 384).

Nitroisopropyl-azobenzene, $C^6H^5.N^2.C^3H^5.NO^2 = N-C^6H^5$
 $N-C(NO^2)(CH^3)^2$, is obtained by adding a solution of diazobenzene nitrate to a recently prepared solution of nitroisopropane in an equivalent quantity of potash-ley, and separates, under the same circumstances as the ethyl-compound, in the form of a yellow oil, which, however, does not solidify. It is transparent, has a golden-yellow colour, sinks in water, is not volatile either alone or with vapour of water, and is distinguished from all the preceding compounds by being quite insoluble in alkalis (Meyer a. Ambühl, *ibid.* viii. 1076).

Derivatives of Amidazobenzene.

Amidazobenzene, or **Amidodiphenylimide**, $C^{12}H^8(NH^2)N^2 = C^6H^5-N=N-C^6H^5(NH^2)$, is produced by a molecular transformation of the isomeric compound diazoamidobenzene, $C^6H^5-N=N-NH(C^6H^5)$, which takes place when the latter is left in contact with alcohol and aniline, or a salt of aniline, especially the hydrochloride. Now diazoamidobenzene is formed by the action of aniline on a solution of diazobenzene nitrate, and a small quantity of aniline or one of its salts is sufficient to effect its conversion into amidazobenzene: hence this transformation takes place to a certain extent in the preparation and in all the decompositions of diazoamidobenzene, since in these reactions aniline is always set free (*1st Suppl.* 271).

In like manner, by treating diazobenzene nitrate with secondary and tertiary amines, as dimethylamine, diethylamine, dimethylaniline, diethylamidobenzoic acid,

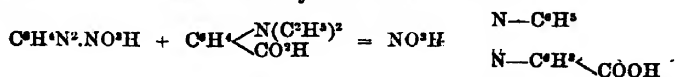
$N \begin{Bmatrix} C^2H^5 \\ C^2H^5 \\ C^2H^5.CO^2H \end{Bmatrix}$, &c., substituted amidazobenzenes are produced containing $N(CH^3)^2$,

&c., in place of NH^2 , and—when substituted amidobenzoic acids are employed—likewise CO^2H in place of an atom of hydrogen (Griess, *Deut. Chem. Ges. Ber.* x. 525).

Azobenzene-dietramidocarbonyl-benzene, $C^{11}H^{11}N^2O^2 = N-C^6H^5$

$N-C^6H^5 \begin{Bmatrix} COOH \\ N(C^2H^5)^2 \end{Bmatrix}$.—This compound is formed in almost theoretical quantity by

mixing a concentrated aqueous solution of 1 mol. diazobenzene nitrate with a cold saturated solution of 2 mols. metadiethylamidobenzoic acid:—



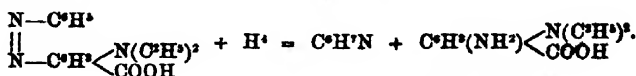
The mixture immediately turns red, and a large portion of the azobenzene-compound separates at once in fine crystals, while the remainder may be obtained from the mother-liquor by spontaneous evaporation.

The compound is moderately soluble in boiling alcohol, and crystallises therefrom in ruby-coloured rhombic or six-sided laminae, with violet surface shimmer. It is but slightly soluble in alcohol and ether, and quite insoluble in water, even at the boiling heat. When gently heated in a test-tube it melts to a yellow-red oil which decomposes with detonation at a higher temperature. In capillary tubes it melts at 125° .

With bases, azobenzene-dietramidocarbonyl-benzene behaves like a monobasic acid. Its *barium salt*, $(C^{11}H^{11}N^2O^2)Ba$, (at 110°), separates in short reddish yellow needles on mixing a moderately dilute ammoniacal solution of the acid with barium

chloride. The *silver salt*, $C^6H^4N^2O^2Ag$, is a deep blood-red, scarcely crystalline precipitate.

Azobenzene-diethamidocarboxyl-benzene does not appear to unite with acids. It is dissolved with deep blood-red colour even by dilute mineral acids, at least with the aid of heat, but separates again from these solutions on addition of water. It decomposes when its hydrochloric acid solution is heated for some time on the water-bath. By reducing agents, as tin and hydrochloric acid or ammonium sulphide, it is decomposed, with assumption of hydrogen, yielding aniline and amido-diethamidobenzoic acid:



Azobenzene-dimethamidocarboxyl-benzene, $\begin{array}{c} N-C^6H^5 \\ || \\ N-C^6H^5 \end{array} \begin{array}{c} N(CH^3)^2 \\ < \\ COOH \end{array}$ —This

compound, produced by the action of metadimethylamidobenzoic acid on diazobenzene nitrate, is also a monobasic acid, and crystallises in dark blood-red needles.

Azocarboxyl-benzene-dimethylamidobenzene, $\begin{array}{c} N-C^6H^5 \cdot COOH \\ || \\ N-C^6H^5 \end{array} \begin{array}{c} N(CH^3)^2 \\ < \end{array}$ —This

acid, isomeric with the preceding, is formed by the action of metadiazobenzoic acid on dimethylaniline. It crystallises from alcohol in yellowish-red nodules.

Azobenzene-dimethamidobenzene, $\begin{array}{c} N-C^6H^5 \\ || \\ N-C^6H^5 \end{array} \begin{array}{c} N(CH^3)^2 \\ < \end{array}$ is a base formed

from diazobenzene and dimethylaniline. It crystallises in delicate yellow laminae melting at 115° , and volatilising in small quantities without decomposition. The hydrochloride forms purple-red capillary needles.

Azosulphoxybenzene-dimethamidobenzene, $\begin{array}{c} N-C^6H^4-SO^2H \\ || \\ N-C^6H^5 \end{array} \begin{array}{c} N(CH^3)^2 \\ < \end{array}$ formed

from dimethylaniline and paradiazophenyl-sulphonic acid (from sulphanilic acid), is a moderately strong acid, and is separated by hydrochloric acid from its boiling alkaline solution in microscopic needles, which, however, soon change to small laminae having a strong violet lustre.

Metazocarboxylbenzene - metadimethamidocarboxylbenzene, $N-C^6H^4-COOH$

$\begin{array}{c} || \\ N-C^6H^5 \end{array} \begin{array}{c} N(CH^3)^2 \\ < \\ COOH \end{array}$ —This acid, produced by the action of metadiazobenzoic acid on

metadimethylamidobenzoic acid, forms a brown-red precipitate gradually becoming crystalline.

All the amidazobenzene-derivatives above described are powerful dye-stuffs (Griess).

Azoxybenzene, $C^6H^5-N^2O = \begin{array}{c} C^6H^5-N \\ C^6H^5-N \end{array} O$.—This compound is obtained when a solution of azobenzene in acetic acid is heated with chromic anhydride to $150^\circ-250^\circ$ in sealed tubes. Repeated treatment with boiling nitric acid (density 1.54), converts it into *trinitroazoxybenzene*, which crystallises in long needles, whilst the addition of water to the mother-liquors causes the separation of a resinous mass, which crystallises from alcohol in long yellow needles, melting at 85° , and having the composition of dinitrobenzene. *Dioxytrinitroazoxybenzene* or *Oxytrinitroazoxybenzene*, $C^6H^3(NO^2)^3N^2O^2$, is obtained by heating a solution of trinitroazoxybenzene in concentrated nitric acid with chromic anhydride for twelve hours to $180^\circ-200^\circ$ in closed tubes; the product is precipitated by water, washed with ether and alcohol, and finally crystallised from nitric acid, benzene, or chloroform. It forms slender needles which melt at 102° . By the further action of the oxidising mixture, *trioxytrinitroazoxybenzene* or *dioxytrinitroazoxybenzene*, $C^6H^2(NO^2)^4N^2O^3$, is produced; it is a yellow crystalline mass which melts at 52° , explodes when heated, and dissolves easily in chloroform or ether (Petrie, *Deut. Chem. Ges. Ber.* vi. 557).

Monoxazobenzene, $O^6H^4-N=N-OC^6H^5$ (2nd Suppl. 151).—This compound, isomeric with azoxybenzene, crystallises in brick-red rhombic prisms, which melt at 150° , and dissolves in toluene and in dilute alcohol, sparingly in boiling water. The addition of silver nitrate to its ammoniacal solution produces a flocculent precipitate which becomes crystalline on standing. The action of nitric acid converts monoxazobenzene into picric acid. *Benzoylazobenzene*, $C^{12}H^8N^2O(C^6H^5O)$, crystallises in plates

or tetrahedrons which melt at 136° , and are easily soluble in toluene, less so in ether, and sparingly in alcohol. *Oxyazobenzenesulphonic acid*, $C^{12}H^9N^2O(HSO^3)$, prepared by the action of fuming sulphuric acid on oxyazobenzene, crystallises in well-formed octohedrons, which are easily soluble in water. The barium-compound crystallises in golden-yellow scales containing 2 mols. water. The easily soluble copper and magnesium compounds crystallise with $3H^2O$; the potassium salt is anhydrous (Tschirvinsky, *ibid.* 560).

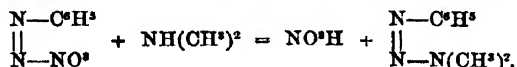
Dichlorazoxybenzene, $C^6H^4Cl-N \begin{array}{c} \diagup \\ \diagdown \end{array} O$ (called in the original paper *Dichloroxyazobenzol*), is formed by heating metachloronitrobenzene with alcoholic potash, and crystallises from alcohol in brilliant, pale yellow, long, flat needles, which melt at 97° , sublime at 180° , and explode when more strongly heated. It is insoluble in water, but soluble in ether, hot crystallisable acetic acid, alcohol, carbon sulphide, and benzene (Laubenheimer a. Winther, *Deut. Chem. Ges. Ber.* viii. 1623).

Dichlorhydrazobenzene, $C^6H^4Cl-NH \begin{array}{c} | \\ | \end{array}$, is formed by boiling dichlorazoxybenzene with ammonium sulphide, and separates from alcohol in small, brilliant, colourless crystals, which melt at 94° , dissolve easily in alcohol and ether, and with yellow colour in strong sulphuric acid. On heating its alcoholic solution with ferric chloride, it is converted into dichlorazobenzene, $C^6H^4Cl-N \begin{array}{c} | \\ | \end{array}$, which crystallises from alcohol in long orange-coloured needles melting at 101° , and dissolving in strong sulphuric acid with deep yellow colour.

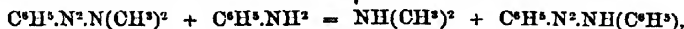
Dichlorhydrazobenzene, warmed with hydrochloric acid, forms dichlorodiamidodiphenyl, $C^6H^4Cl-NH^2 \begin{array}{c} | \\ | \end{array}$, which crystallises from alcohol in small flat prisms melting at 163° , and forms a platinumchloride, $C^{12}H^4Cl^2(NH^2)^2 \cdot 2HCl + PtCl_4$, very sparingly soluble in water and decomposing when heated therewith (Laubenheimer).

Diazobenzene Compounds.

Diazobenzene-dimethylamide, $C^6H^5-N=N-(CH^3)^2$, is obtained by mixing the aqueous solutions of diazobenzene nitrate and dimethylamine:



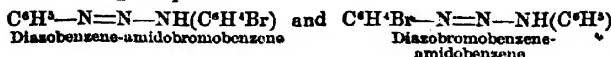
It is a yellowish oil which may be distilled in small quantities without decomposition, but explodes, with liberation of dimethylamine, when heated in larger quantities. It volatilises with vapour of water, is insoluble in water and in alkalis, but dissolves easily in ether, alcohol, and acids. Its alcoholic solution, mixed with *aniline hydrochloride*, gradually decomposes, with formation of dimethylamine and amidazobenzene. [The first product of this reaction is doubtless diazo-amidobenzene:



which is afterwards converted, by molecular transposition, into the isomeric compound amidazobenzene, $C^6H^5.N^2.C^6H^5(NH^2)$.] The aqueous solutions of most of its salts decompose after a short time, with production of phenol, dimethylamine, and nitrogen. The *picrate*, $C^6H^5.N^2.N(CH^3)^2.C^6H^5(NO^2)^3O$, forms yellow needles slightly soluble in ether (Baeyer a. Jäger, *Deut. Chem. Ges. Ber.* viii. 893).

Diazobenzene-ethylamide, $C^6H^5-N=N-NH(C^2H^5)$, probably identical with Griess's *ethyl-diazobenzeneimide*, is prepared in like manner by the action of diazobenzene nitrate on ethylamine, and reacts in like manner with aniline hydrochloride in alcoholic solution, yielding amidazobenzene and ethylamine (Baeyer a. Jäger).

The formulae assigned to the two diazo-amidobenzene-compounds above-described are in accordance with Kekulé's formula of diazo-amidobenzene, $C^6H^5-N=N-NH(C^6H^5)$ (1st *Suppl.* 208). Griess, however, objects to this formula, on the ground that it represents the following compounds:—



formed respectively by the action of diazobenzene nitrate on *p*-bromaniline, and of diazo-

Substitution-derivatives of Benzene—continued.

Abbreviated symbol of compound	Physical properties	Positions of the Substituted Radicles					
		1	Ortho 2	Meta 3	Para 4	Meta 5	Ortho 6
NO ² .I	M. p. 49·4°	NO ²	I	—	—	—	—
—	" 36°; b. p. 280°	NO ²	—	I	—	—	—
—	" 171°	NO ²	—	—	I	—	—
NH ² .NH ²	Four-sided tablets; m. p. 102°;	NH ²	NH ²	—	—	—	—
—	b. p. 252°	—	—	—	—	—	—
—	Crystalline mass; m. p. 63°;	NH ²	—	NH ²	—	—	—
—	b. p. 287°	—	—	—	—	—	—
—	Reddish scales; m. p. 147°;	NH ²	—	—	NH ²	—	—
—	b. p. 267°	—	—	—	—	—	—
NH ² .Br	Needles; m. p. 31·5°; b. p. 229°	NH ²	Br	—	—	—	—
—	Crystalline mass; m. p. 18·5°;	NH ²	—	Br	—	—	—
—	b. p. 251°	—	—	—	—	—	—
—	Rhombic octohedrons; m. p. 64°;	NH ²	—	—	Br	—	—
—	decomposed by heat	—	—	—	—	—	—
NH ² .Cl	Liquid above -14°; b. p. 207°	NH ²	Cl	—	—	—	—
—	Liquid; b. p. 230°	NH ²	—	Cl	—	—	—
—	Rhombic crystals; m. p. 70°-71°;	NH ²	—	—	Cl	—	—
—	b. p. 230°	—	—	—	—	—	—
NH ² .I	Silvery laminæ; m. p. 25°	NH ²	—	I	—	—	—
—	Colourless needles; m. p. 60°	NH ²	—	—	I	—	—
NH ² .NO ²	Dark yellow needles; m. p. 71·5°	NH ²	NO ²	—	—	—	—
—	Long yellow prisms; m. p. 109·9°	NH ²	—	NO ²	—	—	—
—	Orange needles; m. p. 146°	NH ²	—	—	NO ²	—	—
Br.Br.Br	Rhombic plates; m. p. 87·4°;	Br	Br	Br	—	—	—
—	easily sublimable	—	—	—	—	—	—
—	Needles; m. p. 44°; b. p. 275°	Br	Br	—	Br	—	—
—	Rhombic plates; m. p. 119·6°;	Br	—	Br	—	Br	—
—	b. p. above 278°	—	—	—	—	—	—
Cl.Cl.Cl	Large plates; m. p. 53°-54°;	Cl	Cl	Cl	—	—	—
—	b. p. 218°-219°	—	—	—	—	—	—
—	Crystals; m. p. 16°; b. p. 213°	Cl	Cl	—	Cl	—	—
—	Needles; m. p. 63·5°; b. p. 208·5°	Cl	—	Cl	—	Cl	—
NO ² .Br.Br	Yellow tablets; m. p. 61·6°	NO ²	Br	—	Br	—	—
—	Pale greenish yellow needles or	NO ²	—	Br	Br	—	—
—	prisms; m. p. 68·6°	—	—	—	—	—	—
—	Yellow green tablets; m. p. 85·4°	NO ²	Br	—	—	Br	—
—	Thin plates; m. p. 104·5°	NO ²	—	Br	—	Br	—
—	Prisms; m. p. 82·6°	NO ²	Br	—	—	—	Br
NO ² .Cl.Cl	Long needles; m. p. 32·2°	NO ²	Cl	—	Cl	—	—
—	Prisms or tablets; m. p. 55°	NO ²	Cl	—	—	Cl	—
—	Long needles; m. p. 43°	NO ²	—	Cl	Cl	—	—
—	Laminæ; m. p. 64°-65°	NO ²	—	Cl	—	Cl	—
NO ² .Cl.Br	Long needles; m. p. 46·8°	NO ²	Cl	—	Br	—	—
—	Crystals; m. p. 68·6°	NO ²	Cl	—	—	Br	—
—	Yellow-green needles; m. p. 49·5°	NO ²	Br	—	—	Cl	—
—	Long needles; m. p. 82·5°	NO ²	—	Cl	—	Br	—
NO ² .Cl.I	Large prisms; m. p. 63·4°	NO ²	I	—	Cl	—	—
—	Similar, but lighter in colour	NO ²	Cl	—	I	—	—
—	Spherical groups of needles;	NO ²	I	—	—	Cl	—
—	m. p. 63·3°	—	—	—	—	—	—
NO ² .Br.I	Deep yellow crystals; m. p. 83·5°	NO ²	I	—	Br	—	—
—	Yellow crystals; m. p. 126·8°	NO ²	Br	—	I	—	—
—	Large prisms; m. p. 106°	NO ²	—	Br	I	—	—
—	Crystals; m. p. 90·4°	NO ²	I	—	—	Br	—
NO ² .I.I	Quadratic octohedrons; m. p.	NO ²	I	—	I	—	—
—	168·4°	—	—	—	—	—	—
NO ² .NO ² .Br	Yellow prisms or tablets; m. p.	NO	NO ²	—	Br	—	—
—	59·4°	—	—	—	—	—	—
—	Large crystals; m. p. 75·3°	NO ²	—	NO ²	Br	—	—

Substitution-derivatives of Benzene—continued.

Abbreviated symbol of compound	Physical properties	Positions of the Substituted Radicles					
		1	Ortho 2	Meta 3	Para 4	Meta 5	Ortho 6
NO ² .NO ² .Cl	Trimorphous; m. p. 36.3°–38.8°	NO ²	NO ²	—	Cl	—	—
—	Prisms; m. p. 53.4°	NO ²	—	NO ²	Cl	—	—
NO ² .NO ² .I	Yellow prisms or tablets; m. p. 88.5°	NO ²	—	NO ²	I	—	—
—	Orange-coloured rhombic tablets; m. p. 113.7°	NO ²	I	NO ²	—	—	—
NH ² .NH ² .NH ²	Crystalline mass; m. p. 103°; b. p. 330°	NH ²	NH ²	—	NH ²	—	—
NH ² .Br.Br	Colourless needles; m. p. 79.4°	NH ²	Br	—	Br	—	—
—	Silky prisms; m. p. 51°–52°	NH ²	Br	—	—	Br	—
—	Colourless needles; m. p. 80.4°	NH ²	—	Br	Br	—	—
NH ² .Cl.Cl	White needles; m. p. 56.5°	NH ²	—	Br	—	Br	—
—	M. p. 23°–24°; b. p. 250°	NH ²	Cl	Cl	—	—	—
—	Flexible needles; m. p. 62.5°; b. p. 245°	NH ²	Cl	—	Cl	—	—
—	Colourless needles; m. p. 50°	NH ²	Cl	—	—	Cl	—
—	Crystalline; m. p. 71.5°; b. p. 272°	NH ²	—	Cl	Cl	—	—
—	Long needles; m. p. 50.5°	NH ²	—	Cl	—	Cl	—
NH ² .NO ² .NO ²	Light yellow prisms; m. p. 182°–183°	NH ²	NO ²	—	NO ²	—	—
—	Dark yellow needles; m. p. 138°	NH ²	NO ²	—	—	—	NO ²
NH ² .Br.NO ²	Canary-yellow needles; m. p. 104.5°	NH ²	Br	—	NO ²	—	—
—	Felted orange needles; m. p. 111.4°	NH ²	NO ²	—	Br	—	—
—	Reddish-yellow needles; m. p. 151.4°	NH ²	NO ²	—	—	Br	—
NH ² .Cl.NO ²	Light yellow needles; m. p. 104°–105°	NH ²	Cl	—	NO ²	—	—
—	Orange-yellow needles; m. p. 116.4°	NH ²	NO ²	—	Cl	—	—
—	Easily soluble needles; m. p. 117°–119°	NH ²	Cl	—	—	NO ²	—
—	Yellow needles; m. p. 124°–125°	NH ²	NO ²	—	—	Cl	—
—	Yellow laminae; m. p. 123°–157°	NH ²	—	Cl	NO ²	—	—
NH ² .I.NO ²	Steel-blue needles not melting at 220°	NH ²	NO ²	—	—	I	—
Br.Br.Br.Br	Needles; m. p. 137°–140°	Br	Br	—	Br	Br	—
—	Crystals; m. p. 98.5°	Br	—	Br	Br	Br	—
Cl.Cl.Cl.Cl	Needles; m. p. 45°–46°; b. p. 254°	Cl	Cl	Cl	Cl	—	—
—	Needles; m. p. 137°–138°; b. p. 243°–246°	Cl	Cl	—	Cl	Cl	—
—	Needles; m. p. 50°; b. p. 248°	Cl	—	Cl	Cl	Cl	—
NO ² .Br.Br.Br	Rhombic tablets subliming at 187°	NO ²	Br	Br	—	—	Br
—	Crystals; m. p. 112°	NO ²	—	Br	Br	Br	—
—	Yellow needles; m. p. 93.5°	NO ²	Br	—	Br	Br	—
—	Slender needles; m. p. 119.5°	NO ²	Br	Br	—	Br	—
—	Large prisms; m. p. 125°	NO ²	Br	—	Br	—	Br
NO ² .Cl.Cl.Cl	Slender needles; m. p. 58°; b. p. 273°	NO ²	Cl	—	Cl	Cl	—
NO ² .NO ² .NO ² .Cl	Needles; m. p. 83°	NO ²	NO ²	—	—	Cl	—
NH ² .Br.Br.Br	Crystalline; not melting at 130°	NH ²	—	Br	Br	Br	—
—	Long needles; m. p. 118°	NH ²	Br	—	Br	—	Br
NH ² .Cl.Cl.Cl	Colourless needles; m. p. 96.5°; b. p. 270°	NH ²	Cl	—	Cl	Cl	—
—	Needles; m. p. 77.5°; b. p. 260°	NH ²	Cl	—	Cl	—	Cl

Substitution-derivatives of Benzene—continued.

Abbreviated symbol of compound	Physical properties	Positions of the Substituted Radicles					
		1	Ortho 2	Meta 3	Para 4	Meta 5	Ortho 6
$\text{NH}^2.\text{NO}^2.\text{NO}^2.\text{NO}^2$	Orange-red needles or tablets; m. p. 188°	NH^2	NO^2	—	NO^2	—	NO^2
$\text{NH}^2.\text{Br}.\text{Br}.\text{NO}^2$	Light yellow needles; m. p. 202.5°	NH^2	Br	—	NO^2	—	Br
—	Orange needles; m. p. 127.3°	NH^2	Br	—	Br	—	NO^2
$\text{NH}^2.\text{Cl}.\text{Cl}.\text{NO}^2$	Yellow needles; m. p. 66.4°	NH^2	Cl	—	NO^2	Cl	—
—	Orange-red needles; m. p. 100°	NH^2	Cl	—	—	Cl	NO^2
$\text{NH}^2.\text{Cl}.\text{Br}.\text{NO}^2$	Orange-yellow needles; m. p. 106.4°	NH^2	Br	—	NO^2	—	Cl
$\text{NH}^2.\text{NH}^2.\text{Cl}.\text{Cl}$	Long needles; m. p. 60.5°	NH^2	—	Cl	NH^2	Cl	—
$\text{NH}^2.\text{NH}^2.\text{Br}.\text{NO}^2$	Yellow or orange prisms; m. p. 156°	NH^2	Br	—	NH^2	NO^2	—
—	Orange-red needles; m. p. above 150°	NH^2	NO^2	NH^2	—	Br	—

Relations in Physical Properties of the Isomeric Benzene-Derivatives.—Similarly constituted nitrochloro-, nitrobromo-, and nitroiodo-derivatives of benzene exhibit a striking resemblance in all their physical and chemical properties; thus the corresponding chloro- and bromo-derivatives are regularly isomorphous, and isomorphism also exists (although not always) between them and the iodo-derivatives.

Again, colour often affords an important means of judging of the constitution of these bodies, those which are analogous in constitution resembling each other closely in colour; the colour increases in intensity on passing from the chloro- to the bromo-derivative, and thence to the iodo-derivative. This applies not only to the immediate derivatives of benzene, but also to the derivatives of aniline and phenol and the metallic derivatives of the latter. The compounds containing the NO^2 -group in the ortho-position (1 : 2) relatively to an atom of chlorine, bromine, iodine, hydroxyl, or amidogen, are especially characterised by their deep colour: orthonitrochlorobenzene, orthonitrobromobenzene, orthonitroiodobenzene, orthonitrophenol, and orthonitraniline are illustrations of this. The same intensity of colour is exhibited by some tri-derivatives, such as β -dinitroiodobenzene, β -dinitrophenol, and β -dinitraniline, which respectively contain two NO^2 -groups each in the ortho-position relatively to Cl, OH, or NH^2 . This relation does not obtain, however, when two atoms of chlorine, bromine, or iodine, occur each in the ortho-position relatively to a single NO^2 group, diortho-chloronitrobenzene ($\text{NO}^2 : \text{Cl} : \text{Cl} = 1 : 2 : 6$), and the corresponding diorthobromo- and diorthiodonitrobenzene being colourless. Similarly, orthodinitrobenzene and β -dinitroparadichlorobenzene (p. 185) are almost colourless, each of the nitro-groups in the latter compound being in the ortho-position relatively to an atom of chlorine. Of the nitrodibromobenzenes, nitrometadibromobenzene, ($\text{NO}^2 : \text{Br} : \text{Br} = 1 : 2 : 4$), has the deepest colour, exceeding in intensity that of Sicilian sulphur; nitroparadibromobenzene is the next in order, and then comes probably the nitro-orthodibromobenzene, ($\text{NO}^2 : \text{Br} : \text{Br} = 1 : 3 : 4$), which, however, has not yet been obtained quite pure; the remaining nitrodibromobenzenes are almost or entirely colourless.

In odour and solubility also equally marked analogies exist between corresponding chloro-, bromo-, and iodo-derivatives, the solubility and odour increasing, however, from the iodo- to the bromo- and from the latter to the chloro-derivative.

A gradation is likewise observable in the facility with which chlorine, bromine, and iodine, occupying similar positions in analogous compounds, are displaced by other radicles. The displacement of chlorine is usually effected more readily, in less time, and at a lower temperature, than that of bromine or iodine in the corresponding bromo- and iodo-derivatives, bromine being more readily displaced than iodine. This appears to be a general rule in the case of all nitro- and sulpho-derivatives, and is probably a consequence of the more negative character of chlorine as compared with bromine and iodine.

The boiling points of isomeric bodies exhibit in some cases comparatively simple relations. Thus, whilst in many instances the boiling points of corresponding 1 : 4 and 1 : 3 derivatives differ but slightly, the 1 : 2 derivatives frequently have boiling

points considerably higher or lower than those of the corresponding 1:4 and 1:3 compounds.

More remarkable regularities are exhibited by the melting points. Thus among the di-derivatives, whether they contain similar or dissimilar radicles, (Br.Br, NO².Br, NO².Cl, &c.), the *para*-, or symmetrical modification, has invariably the highest melting point, and the *meta*-modification in most cases melts at a higher temperature than the *ortho*-. The *para*-derivatives are all solid at ordinary temperatures, whereas some of the *ortho*- and *meta*-derivatives are liquid. Among the trichloro- and tribromobenzenes, the symmetrical modifications have the highest melting points, and the unsymmetrical the lowest; and in the series of nitrodichloro- and nitrodibromobenzenes, the symmetrical modifications likewise melt at the highest temperatures, while the unsymmetrical modifications of highest melting point are those which have their two haloid radicles in the *para*-position with regard to each other, (NO²:R:R=1:2:5). Lastly, among the tetrachloro- and tetrabromobenzenes, the symmetrical modifications (1:2:4:5) have also the highest melting points; and in the series of nitrotribromobenzenes, the highest melting point (125°) is exhibited by the modification 1:2:4:6, in which the three bromine-atoms are symmetrically disposed. The general conclusion deducible from all these facts is that *the more symmetrical the constitution of a benzene derivative, the greater is the resistance which it offers to the passage from the solid to the liquid state.*

Influence exercised by the nature of the Displacing Groups in the conversion of Mono-derivatives of Benzene into Di-derivatives.—The results of the action of chlorine, bromine, iodine, nitric acid, and sulphuric acid, on the various mono-derivatives of benzene are given in the following table, the series to which the principal product belongs being indicated by thick figures, and the accessory products by smaller figures.

The radicle which occupies the position 1	Series to which the derivative belongs, resulting from the introduction of				
	Cl	Br	I	NO ²	SO ² H
Cl	1:4 1:2	1:4 1:2	1:4	1:4 1:2	1:4
Br	Displaces the bromine	1:4 1:2	?	1:4 1:2	1:4
I	Displaces the iodine	Displaces the iodine	1:4	1:4 1:2	1:4
OH	1:4 1:2	1:4 1:2 1:3	1:4 1:2 1:3	1:4 1:2	1:4 1:2
NH ²	1:4	1:4	1:4	1:4 1:2	1:4
CH ³	1:4	1:4 1:2 1:3	?	1:4 1:2	1:4 1:2
NO ²	1:3	Displaces the nitro-group	Displaces the nitro-group	1:3 1:2 1:4	1:3 1:2 1:4
SO ² H	?	1:3		1:3 1:2 1:4	1:3 1:2 1:4
COOH	1:3	1:3	1:3	1:3 1:2 1:4	1:3 1:2 1:4

The inferences which may be drawn from this table as to the influence exerted by a given radicle upon the position which a second radicle, the same or different in kind, is caused to occupy, are so obvious as to render special explanation unnecessary. The amount of accessory products formed is in general relatively small, and even in the most favourable cases does not appear much to exceed 40 per cent. of the total product; in those cases in which the 1 : 2 derivative is produced together with the 1 : 4 derivative, the amount of the former is always larger the more violent the reaction.

The amount or value of this orientating influence of a group or radicle already introduced into a benzene-molecule, or the position of an atom or radicle about to enter that same molecule, may be approximately estimated by comparing the relative quantities of the derivatives 1 : 4, 1 : 3 and 1 : 2 actually formed, with those which should have resulted if this peculiar influence had not existed. The latter proportion is easily calculated: for since the position 1 : 2 is identical with 1 : 6, and 1 : 3 identical with 1 : 5, whereas the position 1 : 4 is unique, it is clear that, without the orientating influence under consideration, there should result, in every case of the conversion of a mono- into a di-derivative:

20 per cent. of the total product in the form	1 : 4
40 " " " " " " " " " " " " " " "	1 : 3
40 " " " " " " " " " " " " " "	1 : 2

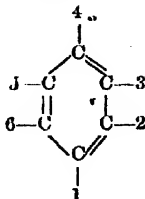
If, then, to take an example, nitric acid of sp. gr. 1.4, acting at a given temperature and in given quantity on monobromobenzene, gives rise to:

67 per cent. nitrobromobenzene in the form	1 : 4
33 " " " " " " " " " " " " " "	1 : 2
0 " " " " " " " " " " " " " "	1 : 3

it follows that the force exerted by an atom of bromine in carrying the group NO^2 to the position 4 must be four times as great as that which carries it to the position 2, and on the other hand the same atom of bromine exercises, with respect to the power of substitution in the position 3, an opposing action completely preventing the formation of the compound 1 : 3, which would otherwise constitute 40 per cent. of the final product.

These considerations are of some importance in determining the conditions which regulate the relative proportions of the several isomerides produced in any of the reactions under consideration, and especially those under which one or the other isomeric modification is produced alone, or disappears altogether from the product.

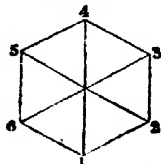
Dependence of the action of the NO^2 -group in favouring the displacement of Chlorine, Bromine, Iodine, &c., on its relative position.—The results obtained by various observers, and especially by Körner, show that an influence is exercised by the NO^2 -group in favouring the displacement of Cl, Br, I, NH^2 , OH, OCH^3 , &c., only when it is in the ortho- (1 : 2) or para- (1 : 4) position relatively to one or other of these radicles (at least in the case of the di- and tri-derivatives), and that it never induces the displacement of these radicles when they occur in the position 3 or 5. Kekulé's original benzene symbol does not afford a satisfactory representation of this; indeed



it rather appears to indicate that the loosening influence exercised by the said NO^2 -group upon a radicle in the position 3 (or 5) is necessarily intermediate between that exercised upon the position 2 and the position 4, which is not actually the case.

This difficulty may, however, be obviated by supposing the six carbon-atoms in the benzene nucleus to be connected as in the annexed figure (1st Suppl. p. 194); that is to say, each carbon-atom directly connected with three others, viz. 1 with 2, 4 and 6; 2 with 1, 3 and 5; 3 with 2, 4 and 6, &c., and generally, each carbon-atom directly connected with those which are in the ortho- and para-positions with respect to it, but not with those which stand to it in the meta-position.

Admitting this mode of connection between the carbon-atoms, it is easy to understand that the NO^2 -group will exercise a greater loosening influence on the atom of

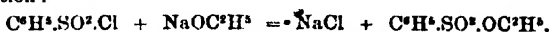


chlorine, bromine, &c., when the atoms of carbon to which this NO^2 -group and the halogen-element, NH^2 -group, or OH -groups &c., stand to one another in the ortho- or para-position, and are therefore directly connected, than when they are in the meta-position, and therefore not directly connected. The same explanation will evidently apply to the direct conversion of mono-derivatives of benzene into di-derivatives under the influence of chlorine, bromine, &c., the di-derivatives thus formed being mostly members of the 1 : 4 and 1 : 2 series, and di-derivatives of these two classes being frequently formed together, whereas the direct formation of meta-derivatives seldom takes place except under the influence of agents of a more energetic or more acid character, strong nitric acid for example. The tendency to the formation of the unsymmetrical modification (1 : 2 : 4 or 1 : 3 : 4) of tri-derivatives in preference to the symmetrical (1 : 3 : 5) or consecutive (1 : 2 : 3) modification, admits also of similar explanation.

Lastly, it may be observed that the mode of connection symbolised in the last figure explains, as well as Kekulé's formula, the existence of only three isomeric di-derivatives of benzene, and the formation of additive compounds, like $\text{C}^6\text{H}^6.\text{Br}^2$ and $\text{C}^6\text{H}^6.\text{Cl}^2$, the chlorine or bromine being supposed to break the connection between the carbon-atoms at the opposite points of the hexagon, so that each carbon-atom remains only singly linked to two other carbon-atoms.

A similar benzene-symbol has been proposed by Körner, in which the six carbon-atoms are supposed to be arranged in two parallel (e.g. horizontal) planes, the atoms 1, 3, 5, in the upper, and 2, 4, 6, in the lower plane, and each atom in the upper plane directly linked to all the three atoms in the lower. Such an arrangement evidently fulfils all the conditions above specified (see *Giornale delle Scienze naturali ed economiche*, v. 241; Palermo, 1869; *Gazzetta chimica italiana*, iv. 444; *Chem. Soc. J.* 1876, i. 241).

BENZENESULPHONIC ACID, $\text{C}^6\text{H}^5.\text{SO}^2\text{H}$. The ethylic ether of this acid is easily produced by the action of benzene sulphochloride on sodium ethylate in alcoholic solution :



It is a yellowish oil with a faint vinous odour, heavier than water, soluble in all proportions in ether, alcohol, and benzene, insoluble in water, and readily decomposed by boiling therewith into alcohol and benzenesulphonic acid (Schiller a. Otto, *Deut. Chem. Ges. Ber.* ix. 1638).

This ether is not produced by the action of alcohol on benzenesulphochloride. Gericke (*Liebig's Annalen*, c. 207) stated that it is formed by heating the lead salt of benzenesulphonic acid with ethyl iodide in sealed tubes, and crystallises in needles easily soluble in water. Schiller a. Otto, however, find that the ether of benzenesulphonic acid is not produced in this manner, or when ethyl bromide is substituted for the iodide; and they suggest that the crystals obtained by Gericke were nothing but benzenesulphonate of lead, which, in fact, dissolves abundantly in ethyl iodide when heated with it under pressure, and crystallises on cooling in small

Nitrobenzenesulphonic Acids, $\text{C}^6\text{H}^4(\text{NO}^2).\text{SO}^2\text{H}$. Laurent obtained an acid of this composition by treating benzenesulphonic acid with nitric acid (v. 564), and similar compounds have been obtained by heating nitrobenzene with fuming sulphuric acid (Schmitt, *Liebig's Annalen*, cxx. 163; Meyer a. Stüber, *ibid.* clxv. 164; H. Rose, *Zeitschr. f. Chem.* 1871, 224); also by heating benzenesulphonic acid, $\text{C}^6\text{H}^5(\text{SO}^2\text{H})$, with fuming nitric acid (1st Suppl. 275), and by heating nitrobenzene dissolved in carbon sulphide with sulphuric hydroxychloride, $\text{SO}^2.\text{OH}.\text{Cl}$ (Armstrong, *Zeitschr. f. Chem.* 1871, 321).

The study of these acids has lately been resumed by Lämpricht (*Liebig's Annalen*, clxxvii. 60), who has obtained, both by Laurent's and by Schmitt's method, the three

modifications of nitrobenzenesulphonic acid, *ortho*-, *meta*-, and *para*-, the *meta*-acid forming by far the larger portion of the product in both cases, but especially in the latter.*

Preparation.—200 grams of pure benzene are mixed in a number of litre flasks, with 800 c.c. of fuming sulphuric acid. The action then begins immediately, with considerable rise of temperature, and may be quickened by agitation, care being taken, however, that the temperature does not rise above the boiling point of benzene. In a few hours the benzene is found to be all dissolved, excepting a small quantity which may be removed with a pipette, after the whole has been poured into a long-necked flask. The benzenesulphonic acid is then poured back into the litre flasks, and nitric acid of sp. gr. 1.54 is added to it by drops, with frequent agitation, the flasks being dipped into cold water at first, and the operation interrupted now and then to moderate the violence of the action. The addition of nitric acid must be continued as long as it occasions any further rise of temperature.

The crude nitrobenzenesulphonic acid is then poured into a large quantity of water, and left in contact therewith till it has become clarified by deposition of a small quantity of dinitrobenzene; then decanted or filtered, neutralised with slaked lime, strained, and concentrated by evaporation, till the calcium salts of the three nitrobenzenesulphonic acids begin to crystallise out.

The salt which separates first still retains a little gypsum, but otherwise consists almost wholly of metanitrobenzenesulphonate; but the following crops of crystals likewise contain the *ortho*- and *para*-modifications in continually increasing proportion. A more complete separation of the three modifications may be effected by converting the calcium salts into the less soluble barium salts; but the best mode of separation is to convert the nitrobenzenesulphonic acids into the corresponding amides, separate these by crystallisation, and then reconvert them into the acids by heating with hydrochloric acid.

For this purpose the first crystallisations of the calcium salt are converted, by treatment with potassium carbonate, into the potassium salt, which is to be dried, pulverised, and converted into the sulphochloride, $C^6H^4(NO^2).SO^2Cl$, by heating it in a basin with an equal weight of phosphorus pentachloride, the mixture being at the same time triturated with a pestle. The mass liquefies at first, but resolidifies on cooling, and is then to be washed with cold water, dissolved in ether, and dehydrated with calcium chloride. The clear decanted solution having been partly freed from ether by distillation, the nitrobenzenesulphochloride crystallises out on standing, in long shining needles melting at 60.5° . This chloride, treated with strong aqueous ammonia, is slowly converted into the corresponding amide, $C^6H^4(NO^2).SO^2NH^2$, which, after washing with cold water and recrystallisation from hot water, with addition of animal charcoal, forms white prisms melting at 161° .

The last crystallisations of the calcium salt, treated in like manner, yield a mixture of three chlorides, two of which are crystalline, but difficult to separate from the third, which is liquid. After washing with water, they are converted by ammonia into an amidated product, separable by repeated crystallisation into three amides, $C^6H^4(NO^2).SO^2NH^2$, melting respectively, at 186° , 161° , and 131° , the second being identical with that above mentioned (*meta*-). The amide with the highest melting point (*ortho*-) is the least soluble, and that with the lowest melting point (*para*-) the most soluble of the three.

These amides heated to 150° , in sealed tubes with strong hydrochloric acid, are converted into the ammonium salts of the corresponding nitrobenzenesulphonic acids, which may be obtained in the pulverulent state by evaporating the resulting solutions to dryness, and converted into barium salts by boiling with baryta-water; and from the latter salts the other nitrobenzenesulphonates, and the free acids, may be obtained by ordinary methods.

The mixture of the three acids obtained by nitration of benzenesulphonic acid, as above, contains about 90 p. c. of the *meta*- (or α -) acid; that obtained by treating nitrobenzene with sulphuric acid contains a still larger proportion of this modification.

Metanitrobenzenesulphonic acid may also be obtained by treating nitrosulphanilic-benzenesulphonic acid (p. 228), suspended in alcohol, with nitrous acid, whereby it is converted into the diazo-compound, and decomposing the latter with absolute alcohol under pressure (Goslich, *Liebigs Annalen*, clxxx. 104).

The following table exhibits a comparative view of the principal properties of the three acids, their salts, chlorides, and amides. The *ortho*- and *para*-acids having been obtained in small quantity only, the investigation of their salts is necessarily less complete than that of the *meta*-acid:

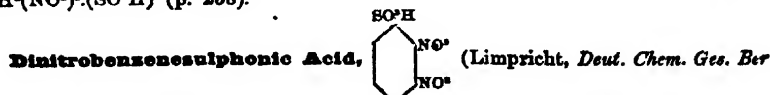
* Limpricht distinguishes the three modifications as α , β , γ . His first experiments did not indeed fix the relative positions of the radicals NO^2 and SO^2H in the three acids. This, however, has been done by Nitting, who has shown, by examination of the corresponding amidobenzenesulphonic acids, that Limpricht's α , β , and γ acids are respectively the *meta*-, *para*-, and *ortho*-modifications, and his experiments have confirmed this result (p. 226).

Benzenesulphonic Acids.

Salts	Ortho (γ)	Meta (α)	Para (β)
$C^6H^4(NO^2).SO^2NH^+$	Long glistening needles.	Transparent brittle prisms.	Transparent plates.
$C^6H^4(NO^2).SO^2K$	Small glistening needles sparingly soluble.	Plates or long needles.	Small prisms.
$C^6H^4(NO^2).SO^2Na$		From water in large square plates.	
$[C^6H^4(NO^2).SO^2]^2Ba$	+ H^2O . Hard, crystalline, very soluble crusts.	+ H^2O . Small prisms or plates (Limpricht); needles (Gölich).	$3H^2O$. Small, very thin plates.
$[C^6H^4(NO^2).SO^2]^2Ca$		+ $2H^2O$. Large white plates.	+ $2H^2O$. White, very soluble needles.
$[C^6H^4(NO^2).SO^2]^2Mg$	— —	+ $4H^2O$. Very soluble white prisms.	— —
$[C^6H^4(NO^2).SO^2]^2Zn$	— —	+ $3H^2O$. Like the magnesium salt.	— —
$[C^6H^4(NO^2).SO^2]^2Pb$	Very soluble transparent four-sided plates.	+ $2H^2O$. Short compact prisms, or tufts of thin needles.	+ $2H^2O$. Globular masses of prisms.
$[C^6H^4(NO^2).SO^2]^2Cu$	— —	Pale green hydrated needles, becoming nearly white when dehydrated.	— —
Chloride: $C^6H^4(NO^2).SO^2Cl$	From ether in white or reddish flat prisms; m.p. 67° .	From ether in transparent four-sided prisms; m.p. 60.5° (Limpricht); 61° (Gölich).	Separates from ether as a red oil.
Amide: $C^6H^4(NO^2).SO^2NH^2$	Thin needles, m.p. 186° ; very slightly soluble in cold, more freely in hot water, very easily in alcohol.	Needles or prisms, m.p. 181° ; slightly soluble in cold, more freely in hot water, very easily in alcohol.	Compact prisms, m.p. 131° ; easily soluble in hot water, more freely in alcohol.

Metanitrobenzenesulphonic acid crystallises from water or alcohol in large deliquescent plates; the other two acids have not been obtained in the free state in definite form. When the three acids are fused with potash, ammonia is evolved and oxalic acid is formed, together with a brown oil. By reduction with alcoholic ammonium sulphide, these acids are converted into the corresponding amidobenzenesulphonic acids, $C^6H^4(NH^2).SO^2H$, the para-modification of which is identical with aniline acid.

Metanitrobenzenesulphonic acid may be boiled, or even heated to 170° , with the strongest nitric acid, without undergoing any change, but a mixture of 2 pts. nitric and 1 pt. sulphuric acid converts it into dinitrobenzene-disulphonic acid, $C^6H^2(NO^2)_2(SO^2H)^2$ (p. 258).



ix. 554; Sachs, *Liebig's Annalen*, clxxxviii. 143). To prepare this acid, pure and dry metanitrobenzenesulphonic acid is mixed in a tubulated retort, with an equal volume of fuming sulphuric acid, and 3 vols. of the strongest nitric acid are gradually added, with frequent agitation, the liquid being gently warmed as soon as the first violent action has subsided, and the nitric acid which distils over, poured back from time to time, fresh quantities being added if necessary. When the conversion of

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mononitro- into the dinitro-acid (which requires from fourteen to sixteen days' boiling) is nearly complete, the contents of the retort are diluted with water, and evaporated in a basin over the water-bath as long as nitric acid continues to be evolved. This operation also takes several days, and the water which evaporates must be replaced from time to time. The liquid is then again diluted with water, neutralised with slaked lime and strained; and the solution which runs through is evaporated, freed from calcium by sulphuric acid and alcohol, then neutralised with barium carbonate and evaporated to the crystallising point. It then usually deposits, first a few nodular crystals of barium metanitrobenzenesulphonate, afterwards red and sometimes rather large crystals of the dinitro-salt; and the mother-liquor, which no longer yields distinct crystals, contains, according to Limpricht, the barium salt of another dinitrobenzenesulphonic acid; according to Sachse, a dinitrophenol, $C^6H^2(NO_2)_2OH$.

The dinitrobenzenesulphonic acid, $C^6H^2(NO_2)_2SO^3H$, separated by sulphuric acid from the pure barium salt, remains on evaporation as a brownish syrup, which solidifies on cooling to a crystalline very deliquescent mass, easily soluble in alcohol.

The ammonium salt, $C^6H^2(NO_2)_2SO^3NH_4$, forms anhydrous lemon-yellow laminae and tablets, having a vitreous lustre, which they lose on exposure to the air; it is moderately soluble in water.

$C^6H^2(NO_2)_2SO^3K + 1\frac{1}{2}H^2O$ crystallises on cooling from a hot solution in light, yellow, glassy, nearly transparent needles an inch long, which quickly effloresce, and become opaque when exposed to the air; moderately soluble in water.

$[C^6H^2(NO_2)_2SO^3]^2Ba + 3H^2O$. Separates from somewhat dilute solutions in isolated well-developed roseate crystals, probably rhombic prisms, modified so as to make them look like quadratic octohedrons. Easily soluble in water.

$[C^6H^2(NO_2)_2SO^3]Pb + 3H^2O$. Separates from a hot solution on cooling in lemon-yellow shining laminae, which on exposure to the air become light-yellow and lose their lustre. Dissolves in water with light yellow colour.

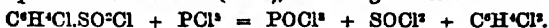
The chloride, $C^6H^2(NO_2)_2SO^3Cl$, separates from solution in ether at a winter temperature, in nodules, which, after several recrystallisations from ether, melt at 89° (Sachse), at 97° (Limpricht).

The amide, $C^6H^2(NO_2)_2SO^3NH_2$, crystallised from hot water with the aid of animal charcoal, forms yellowish, or greenish silky needles, easily soluble in hot, sparingly in cold water, melting at 238° (Sachse), at 255° (Limpricht).

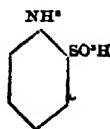
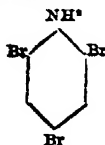
The dinitro-compound may be converted into the diamido-acid, $C^6SO^3H.NH^2.NH^2.H^2$, by reduction either with ammonium sulphide or with tin and hydrochloric acid; and on passing nitrous acid into the solution of this amido-acid in concentrated hydrobromic acid, a dibromobenzenesulphonic acid is obtained, having the constitution $C^6SO^3H.Br.Br.H^2$. Hence the diamido-acid, and the dinitro-acid from which it is formed must also have the constitution 1 : 2 : 3, as represented by the formula given on p. 225 (Sachse).

Amidobenzenesulphonic Acids, $C^6H^2NH^2.SO^3H$ (Limpricht, *Lieber's Annalen*, clxxvii. 79; clxxx. 88; *Deut. Chem. Ges. Ber.* viii. 1065. Berndsen, *Lieber's Annalen*, clxxvii. 82. Berndsen a. Limpricht, *ibid.* 98. Nölting, *Deut. Chem. Ges. Ber.* viii. 1091).

Three modifications of this acid, α , β , γ , are formed by reduction of the corresponding nitrobenzenesulphonic acids (p. 223). Of these, the one designated α or β is identical with the acid long known as sulphanilic acid, produced by the action of sulphuric acid on aniline (v. 477); and this acid is converted by chlorine into a chlorobenzenesulphonic acid, the chloride of which, when treated with phosphorus pentachloride, yields *paradichlorobenzene* (1 : 4), according to the reaction :



Sulphanilic acid is therefore the *para*-modification of amidobenzenesulphonic acid. Now both this and the modification designated γ , are converted by treatment with bromine into ordinary tribromaniline, which, as Körner has shown (p. 195), has the constitution 1 : 2 : 4 : 6 or $C^6.NH^2.Br.H.Br.H.Br$. Consequently, one of these two amidobenzenesulphonic acids must have the groups NH^2 and SO^3H in the 1 : 4 and the other in the 1 : 2 position; thus:—



The 1 : 4 position has, however, been shown to belong to the β -modification, or sul-

phanilic acid; the γ -acid must, therefore, be the 1 : 2 or ortho-modification. For the α -acid there remains, therefore, only the 1 : 3 or meta-constitution (Nörling).

The three amido-acids are converted by the action of nitrous acid into the corresponding diazobenzenesulphonic acids.

These conclusions are corroborated by the result of heating the potassium salts of the corresponding bromobenzenesulphonic acids with dehydrated potassium ferrocyanide. The potassium salt of β -bromobenzenesulphonic acid (obtained either from bromobenzene and sulphuric acid or from sulphanilic acid) is converted by this treatment into a dicyanobenzene, $C_6H_4(CN)_2$, which, when boiled with alcoholic potash, or more readily when heated to 160° with hydrochloric acid, is converted into terephthalic acid; and the potassium salt of α -bromobenzenesulphonic acid (from α -amidobenzenesulphonic acid), treated in a similar manner, yields a dicyanobenzene convertible into isophthalic acid. Consequently, α -amidobenzenesulphonic acid and its congeners belong to the meta-, and the β -acids to the para-series and therefore the γ -acids must belong to the ortho-series (Limpricht, *Liebig's Annalen*, clxxx. 88).

Metamidobenzenesulphonic acid, $C_6H_4NH_2 \cdot H \cdot SO_3H \cdot H^+$ (Berndsen, *loc. cit.*) This acid was first obtained by Laurent, by reduction of nitrosulphobenzonic acid (v. 477). It is prepared by reducing metanitrobenzenesulphonic acid with ammonium sulphide (Berndsen), or by heating bromometamidobenzenesulphonic acid with hydriodic acid in sealed tubes to 120° (Goslich). It usually crystallises in long slender octontrically grouped anhydrous needles; but by very slow separation from aqueous solution at ordinary temperatures, it may be obtained in transparent colourless monoclinic prisms containing $1\frac{1}{2}H_2O$, which they give off slowly with efflorescence. It is sparingly soluble in cold, freely in hot water, insoluble in alcohol and ether. The aqueous solution turns red in contact with the air, and then yields coloured crystals, which, however, become colourless again by recrystallisation in contact with animal charcoal. When heated it decomposes without previous fusion, leaving a slowly burning cinder. It is easily oxidised by sulphuric acid and potassium chromate or manganese dioxide, but does not yield quinone. The *diazo-acid* formed from it by the action of nitrous acid yields, when heated with water, a phenol-sulphonic acid, convertible by fusion with potash into resorcin—a further proof that this acid belongs to the meta-series (2*nd* Suppl. 1110).

Bromine acts immediately on metamidobenzenesulphonic acid in aqueous solution, forming a di- or tribromamidobenzenesulphonic acid, accordingly as 2 or 3 mols. of bromine are added. With more than 3 mols. of bromine, bromanil, $(C_6Br_3O)_2$, is also formed, being the direct product of the action of bromine on the tribrominated acid.

Chlorine in excess passed rapidly into a hot strong solution of the acid colours it red, brown, and finally yellow, and throws down crystals of chloranil, $C_6Cl_4O_2$. The same substance is produced by treating the acid with hydrochloric acid and potassium chlorate, whereby nearly the whole of the sulphur of the amido-acid is eliminated as sulphuric acid. The product of the action of 3 mols. only of chlorine on the amido-acid is dichloramidobenzenesulphonic acid, $C_6H_3Cl_2(NH_2)SO_3H + 2H_2O$, which forms delicate white needles easily soluble in water.

Barium Metamidobenzenesulphonate, $(C_6H_4 \cdot NH_2 \cdot SO_3)^2Ba \cdot 6H_2O$, crystallises in small reddish prisms which dissolve easily in water, and give off the greater part of their water of crystallisation over oil of vitriol. The *lead salt*, $(C_6H_4 \cdot NH_2 \cdot SO_3)^2Pb$, forms rather large reddish six-sided anhydrous prisms, slightly soluble in cold, more freely in hot water.

Orthoamidobenzenesulphonic acid, $C_6H_4NH_2 \cdot SO_3H \cdot H^+$ (Berndsen & Limpricht, *loc. cit.*; Bahlmann, *Liebig's Annalen*, clxxvi. 307).—This acid, prepared by reduction of ortho-nitrobenzenesulphonic acid, is distinguished by the beauty and variety of its crystalline forms. It usually separates in dull white crystals, exactly like rhombohedrons, sometimes also in groups of thick rhombic tablets, intergrown with transparent, colourless, highly lustrous crystals, some more isolated and consisting of four-sided prisms bevelled at both ends with two faces, others exhibiting a larger number of faces. A solution decolorised by animal charcoal deposits, after standing for some time in a closed vessel, colourless or white crystals, and the mother-liquor, concentrated by evaporation, yields crystals of a pure yellow, or light-red to brown-red, and sometimes violet colour, which also may be decolorised by animal charcoal. The crystals of rhombohedral aspect are anhydrous, the transparent shining prismatic crystals have the composition $2C_6H_4(NH_2)(SO_3H) + H_2O$.

The *barium salt*, $(C_6H_4 \cdot NH_2 \cdot SO_3)^2Ba$, forms rather large transparent, colourless, oblique four-sided prisms, with oblique end-faces, anhydrous, and easily soluble in water.

The *lead salt*, $(C_6H_4 \cdot NH_2 \cdot SO_3)^2 \cdot 2Pb + \frac{1}{2}H_2O$, crystallises in small shining six-

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sided laminae, or in larger prisms, sparingly soluble, in water (Berndsen a. Limp-richt).

The *potassium salt*, $C^6H^4(NH^2)SO^3K + 5H^2O$, forms large colourless well-defined prisms, very soluble in water. The *silver salt*, $C^6H^4(NH^2)SO^3Ag$ (anhydrous), crystallises in slender, brittle, brownish needles, easily soluble in hot, rather sparingly in cold water. The solution when heated quickly turns dark red (Bahlmann).

The action of bromine on orthamidobenzenesulphonic acid gives rise to the formation of sulphuric acid, tribromaniline, monobromamidobenzenesulphonic acid and dibromamidobenzenesulphonic acid, $C^6SO^3.NH^2.Br.H.Br.H$.

Nitroparamidobenzenesulphonic or Nitrosulphanilic acid,



is produced by heating the corresponding bromonitrobenzenesulphonic acid to 180° with alcoholic ammonia. It is a yellow uncrystallisable solid. The following derivatives have been prepared:—

Potassium salt, $C^6H^3(NH^2)(NO^2)SO^3K + H^2O$.—Warty groups of indistinct yellow crystals. 100 c.c. of the aqueous solution at 6° contain 5.29 grms. of the anhydrous salt.

Ammonium salt, $C^6H^3(NH^2)(NO^2)SO^3NH^4$.—Anhydrous; resembles the potassium salt. 100 c.c. of aqueous solution at 6° contain 13.44 grm. of the salt.

Barium salt, $[C^6H^3(NH^2)(NO^2)SO^3]^2Ba + 2\frac{1}{2}H^2O$.—Deep yellow laminae. 100 c.c. of the aqueous solution at 9° contain 0.5168 grm. of the anhydrous salt.

Lead salt, $[C^6H^3(NH^2)(NO^2)SO^3]^2Pb + 2H^2O$.—Broad yellow needles grouped in tufts. Decomposes at 180° . 100 c.c. of solution at 6° contain 2.087 grm. of the anhydrous salt.

Chloride, $C^6H^3(NH^2)(NO^2)SO^2Cl$.—Crystallises from ether in large light-yellow transparent rhombic crystals melting at 50° – 60° .

Amide, $C^6H^3(NH^2)(NO^2)SO^2NH^2$.—Crystallises from hot water in light yellow slender needles melting at 155° – 156° (Goslich, *Liebigs Annalen*, clxxx. 103).



Diamidobenzenesulphonic acid,



(Sachse, *Liebigs Annalen*,

clxxviii. 148).—This acid may be formed by reduction of the corresponding dinitro-acid (p. 225), either with ammonium sulphide or better with tin and hydrochloric acid. When purified by recrystallisation it separates from solution by slow cooling in large well-defined rhombic tablets, by more rapid cooling in vitreous rhombic prisms often several inches long, with oblique end-faces which reflect light totally; from very strong solution it crystallises in small needles. The crystals when fresh are colourless or slightly yellowish, but often become darker coloured on exposure to the air; the aqueous solution also soon turns brown and afterwards violet. The acid dissolves easily in hot, sparingly in cold water, and is nearly insoluble in alcohol and ether. When heated it decomposes without previous fusion.

The aqueous solution of the acid has a strong acid reaction and decomposes carbonates; but the salts which it forms with bases are by no means well defined, and solidify in coloured, non-crystalline, or scarcely crystalline masses.

With the stronger acids, on the other hand, this diamido-acid forms well-characterised salts.

The *hydrochloride*, $C^6H^4(NH^2)_2SO^3H.HCl$ (anhydrous), separates on cooling from a solution of the diamido-acid in hot concentrated hydrochloric acid in faintly reddish needles, moderately soluble in cold, easily in hot water. The stannoso-chloride, $C^6H^4(NH^2)_2SO^3H.HCl.SnCl^2$ (anhydrous), is formed in the reduction of dinitrobenzenesulphonic acid by tin and hydrochloric acid, and may be purified by recrystallisation from a small quantity of hot water. It then forms small colourless shining needles which, when exposed to the air, lose their lustre and turn yellowish. The aqueous solution reduces mercuric chloride, and gives a black precipitate with hydrogen sulphide.

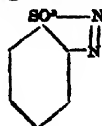
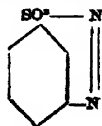
The *hydrobromide*, $C^6H^4(NH^2)_2SO^3H.HBr$ (anhydrous).—Prepared like the hydrochloride. Small shining reddish prisms or long needles.

Sulphates.—The *neutral salt*, $[C^6H^4(NH^2)_2SO^3H]^2.SO^3H^2 + H^2O$, is formed by heating the diamido-acid with sulphuric acid diluted with an equal volume of water

till it dissolves, and separates on cooling in colourless shining tablets, which become opaque when removed from the mother-liquid, and are not easily freed from it, on account of their great solubility in water.

The acid salt, $C^6H^4(NH^2)SO^2H \cdot SO^2H + \frac{1}{2}H^2O$.—Deposited from the mother-liquor of the preceding, after evaporation and cooling, in small transparent four-sided prisms.

DIAZOBENZENESULPHONIC ACIDS, $C^6H^4N^2SO^2$.—Two modifications of this acid, the *meta*- and *ortho*-, are obtained by the action of nitrous acid on the corresponding amido-acids. They are represented by the following formulæ:



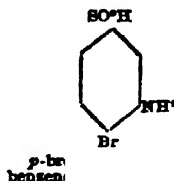
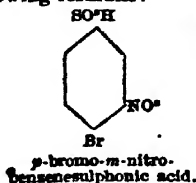
Metadiazobenzenesulphonic acid was first described by Meyer a. Stüber (*Liebig's Annalen*, clxv. 165), who, however, obtained it only in an impure state, mixed with amidobenzenesulphonic acid. To prepare it in the pure state, a hot concentrated solution of metamidobenzenesulphonic acid is left to cool till the acid begins to separate out, and a rapid stream of nitrous acid gas is passed into the pasty mass, the cylinder containing the acid being cooled by immersion in cold water. When the liquid becomes clear, which shows that the action is complete, it is left for twenty-four hours at as low a temperature as possible, and the diazo-acid is separated from the supernatant liquid, freed from adhering liquid by pressure between porous tiles, and further treated while still moist with nitrous acid. When perfectly dry, it is a most dangerous body, exploding with the greatest violence even when stirred with a spatula.

This acid crystallises from water in small reddish-yellow prisms very soluble in water, and decomposing at 60° with rapid evolution of nitrogen. Absolute alcohol does not act upon it at the boiling heat under ordinary pressure. Heated on platinum foil it explodes, leaving a porous slowly combustible cinder; it likewise explodes when struck with a hammer. It is decomposed by hydrobromic acid, forming meta-bromobenzenesulphonic acid, $C^6Br.H.SO^2H.H^+$, together with a bromophenolsulphonic acid (Berndsen, *Liebig's Annalen*, clxxvii. 88).

Orthodiazobenzenesulphonic acid is formed by passing nitrous acid gas into water in which the finely pulverised ortho-amido-acid is suspended, the pulverulent precipitate quickly changing to laminar crystals, which sparkle brilliantly in the liquid as they are stirred up by the gas-stream. Under the microscope they appear as rhombic plates; and larger yellowish crystals of the same shape are deposited when the liquid, filtered from the tabular crystals, is left to stand in the cold. The crystals detonate sharply when heated on platinum-foil, and give off nitrogen when boiled with water. The acid mixed with hydrobromic acid and evaporated, is converted into orthobromobenzenesulphonic acid, $C^6.Br.SO^2H.H^+$ (Berndsen a. Limpricht, *ibid.* 101).

Bromamidobenzenesulphonic Acids. (1.) The *monobrominated acid*, $C^6H^3Br(NH^2).SO^2H$, obtained by reducing the ammonium salt of nitroparabromobenzenesulphonic with ammonium sulphide, forms a white indistinctly crystalline powder, containing $1\frac{1}{2}$ mol. water of crystallisation; sparingly soluble in cold, more easily in hot water. Its barium and calcium salts are non-crystalline powders, nearly insoluble in water.

On heating this bromamidated acid with hydriodic acid to 120° – 130° , the bromine is replaced by hydrogen and *metanitrobenzenesulphonic acid* is produced. Hence this bromamido-acid and the corresponding bromonitro-acid are represented by the following formulæ:



(Goslich, *Deutsch. Chem. Ges. Ber.* viii. 353; *Liebig's Annalen*, clxxx. 100).

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(2). *Metabromorthamidobenzenesulphonic acid*, $\text{C}^6\text{H}_4\text{SO}_3\text{H.NH}^2\text{.H.H.Br.H}$ (Limpricht, *Liebig's Annalen*, clxxxi. 196; Thomas, *ibid.* clxxxvi. 126; Bahlmann, *ibid.* clxxxvi. 310; Borns, *ibid.* clxxxvii. 368).—This acid is produced: 1. Together with other products, by the action of bromine on orthamidobenzenesulphonic acid or its barium salt. Bromine (1 mol.) is slowly dropped, with agitation, into a very dilute and cooled solution of barium orthamidobenzenesulphonate, whereupon the colour of the bromine immediately disappears, and a precipitate is formed, consisting of barium sulphate and tribromanilino. The liquid, heated to the boiling point, neutralised with barium carbonate, and filtered hot, deposits, on cooling and evaporation, first, dibromamidobenzenesulphonate of barium in small well-defined crystals, then the monobromamidobenzenesulphonate in thin laminae, and finally amidobenzenesulphonate and bromide of barium. The monobromamidobenzenesulphonate, purified by a few recrystallisations, and decomposed by dilute sulphuric acid, yields the free monobromamidobenzenesulphonic acid, to which, however, a certain quantity of amidobenzenesulphonic acid still obstinately adheres. The separation of the latter is best effected by stirring up the mixture with water at $60^\circ\text{--}70^\circ$, decanting from the undissolved amido-acid, and filtering off the solution, cooled to about 30° , from bromamido-acid, which then separates out. The acid thus obtained is pressed and recrystallised from water till the solution no longer turns red, an effect which indicates the presence of unaltered amidobenzenesulphonic acid (Limpricht; Bahlmann).

2. By reducing the corresponding nitro-acid with ammonium sulphide, or better with tin and hydrochloric acid. The metal and acid are heated together till hydrogen begins to escape, and the concentrated solution of the nitro-acid is then added. The liquid soon becomes colourless, and on cooling deposits the bromamido-acid as a white crystalline mass. The liquid filtered therefrom and freed from tin by hydrogen sulphide, yields on evaporation an additional quantity of the amido-acid, which may be purified by crystallisation from hot water, with the aid of animal charcoal (Thomas).

3. By the action of fuming sulphuric acid on parabromacetanilide. This substance—prepared either by adding bromine-water to acetanilide suspended in a large quantity of water, or by adding the calculated quantity of bromine to a solution of acetanilide in glacial acetic acid—is heated to $170^\circ\text{--}180^\circ$ for several hours in a porcelain basin, with an equal weight of fuming sulphuric acid, whereupon acetic acid is evolved; the viscid mass, which gives off large quantities of sulphurous acid, is stirred up with water after cooling; and the undissolved bromamidobenzenesulphonic acid is purified by recrystallisation from hot water, with addition of animal charcoal. The bromamido-acid remaining in the liquid may be obtained by neutralising with slaked lime, evaporating the filtrate, and decomposing the calcium salt with sulphuric acid. The bromamido-acid obtained by this process is sometimes contaminated with bromaniline; in that case it must be evaporated down with baryta-water till all the bromaniline is volatilised, and the resulting barium salt decomposed with sulphuric acid (Borns).

This bromamidobenzenesulphonic acid crystallises in long slender white silky needles, containing $1\text{H}^2\text{O}$, or in large thick light brown slowly efflorescent prisms, with $2\text{H}^2\text{O}$ (Borns). It is slightly soluble in cold, easily in hot water, nearly insoluble in alcohol; burns away when heated on platinum foil, without previous fusion.

Ammonium salt, $\text{C}^6\text{H}_4\text{Br}(\text{NH}^2).\text{SO}^3\text{NH}^4$ (anhydrous).—Small reddish easily soluble crystals (Borns).

Potassium salt, $\text{C}^6\text{H}_4\text{Br}(\text{NH}^2).\text{SO}^3\text{K}$ (anhydrous).—Transparent laminae or prisms easily soluble in water (Thomas, Borns).

Barium salt, $[\text{C}^6\text{H}_4\text{Br}(\text{NH}^2).\text{SO}^3]_2\text{Ba} + \text{H}^2\text{O}$.—Colourless nacreous prisms or laminae, which turn red in the moist state and dissolve easily in water and in dilute alcohol (Limpricht, Thomas, Borns).

Calcium salt, $[\text{C}^6\text{H}_4\text{Br}(\text{NH}^2).\text{SO}^3]_2\text{Ca} + \text{H}^2\text{O}$.—Small prisms very soluble in water.

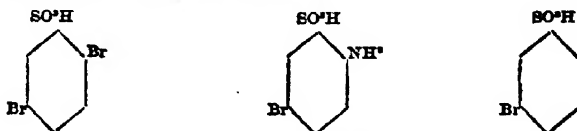
Lead salt, $[\text{C}^6\text{H}_4\text{Br}(\text{NH}^2).\text{SO}^3]_2\text{Pb} + 2\text{H}^2\text{O}$.—Well-defined long flat needles, mostly pointed, less soluble in water than the other salts (Thomas).

The *chloride*, formed by gently heating the potassium salt with PCl^5 , separates as an oil on addition of water, but decomposes somewhat rapidly during washing with water, the wash-water after a while depositing fine crystals of the acid (Borns).

The *diaso-compound*, $\text{C}^6\text{H}_4\text{Br} \begin{smallmatrix} \text{N}^2 \\ \text{SO}^3\text{H} \end{smallmatrix}$, formed by passing nitrous acid into a small quantity of strong alcohol in which the bromamido-acid is suspended, forms needles which turn red on exposure to light. It explodes when heated or struck, dissolves readily in water, but quickly decomposes in the solution; dissolves somewhat sparingly in alcohol (Borns).

This diaso-compound is converted by the action of hydrobromic acid into *para*-

dibromobenzenesulphonic acid, and by boiling with absolute alcohol into metabromobenzenesulphonic acid. These reactions establish the constitution of the bromamido-acid, as shown by the following formula:—



Orthobromometamidobenzenesulphonic acids, $C^6H^3Br(NH^2)SO^3H$ (Bahlmann, *Liebig's Annalen*, clxxxii. 318, 322).—Orthobromobenzenesulphonic acid, treated with very strong nitric acid, yields two nitrobrominated acids, $C^6H^2Br(NO)^2SO^3H$, which may be separated by means of their barium salts, one of which, constituting the principal product, crystallises in needles, while the other, which is the more soluble of the two, crystallises in laminae. The acids separated from these barium salts yield, by reduction with tin and hydrochloric acid, the corresponding bromamidated acids.

a. The bromamido-acid obtained from the nitro-acid yielding the acicular barium salt, separates from a concentrated aqueous solution in slender white anhydrous needles, easily soluble in hot, sparingly in cold water, insoluble in alcohol and in ether.

hedrons, containing $2H^2O$, which easily effloresce, and may be converted by recrystallisation into the anhydrous needles.

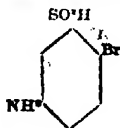
The following salts were obtained by neutralisation with the respective carbonates:—

$[C^6H^3Br(NH^2)SO^3]^2Ba + 2H^2O$. The solution of the acid neutralised with barium carbonate becomes deep red on evaporation, and solidifies when highly concentrated to a radio-crystalline mass. The salt, when freed from mother-liquor by pressure, dissolves very easily in water and in alcohol.

$[C^6H^3Br(NH^2)SO^3]^2Pb$. Separates from solution after nearly all the water has been evaporated, as a brownish indistinctly crystalline mass, which redissolves very easily in water.

$C^6H^3Br(NH^2)SO^3Ag$. The neutral solution quickly turns red, and deposits the salt in nodular groups of small brown needles.

The relative positions of the NH^2 and Br in this acid are determined by the following reactions: (1). By heating the acid with hydriodic acid and phosphorus, the bromine-atom is removed, and metamidobenzenesulphonic acid is produced; (2). By converting the bromamido-acid into the corresponding diazo-compound, and heating the latter with hydrobromic acid, paradibromobenzenesulphonic acid is obtained. The first reaction shows that the NH^2 -group is in the meta-position with regard to the SO^3H , and the second that the bromine-atom in the original acid is in the para-position with regard to the NH^2 , and therefore in the ortho-position with respect to the SO^3H . The acid is therefore metamidorthobromobenzenesulphonic acid:



β. The bromamido-acid formed from the nitro-acid yielding the laminar barium salt, as above mentioned, crystallises in well-defined yellowish pointed prisms, sparingly soluble in cold, easily in hot water; when heated it chars without previous fusion. Its barium salt, $[C^6H^3Br(NH^2)SO^3]^2Ba + xH^2O$, forms small indistinct nodules easily soluble in water and alcohol.

Attempts to determine the structure of this acid—which was obtained in small quantity only—did not yield definite results.

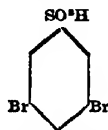
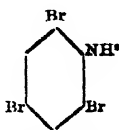
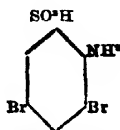
Dibromamidobenzenesulphonic Acids, $C^6H^2(NH^2)Br^2SO^3H$. (1). *Dibromorthamidobenzenesulphonic acid*, $C^6H^2SO^3H.NH^2.Br.H.Br.H$ (Berndsen & Limpricht, *Liebig's Annalen*, clxxvii.; Limpricht, *ibid.* clxxxi. 198; *Deut. Chem. Ges. Ber.* viii. 1429).—When bromine is added to a solution of orthamidobenzenesulphonic acid or its barium salt, a precipitate is formed containing—together with a little tribrom-aniline and barium sulphate—dibromorthamidobenzenesulphonic acid or its barium salt, the greater part of which remains in solution, and may be separated therefrom by evaporation. Both the free acid and its barium salt are but sparingly soluble in water, and therefore easily purified.

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The *free acid* crystallises in crusts of thick rhombic tables, or by slow evaporation from dilute solutions in four-sided prisms containing 4 mol. H_2O . The *potassium salt*, $\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}^-\text{K} + \text{H}_2\text{O}$, forms easily soluble transparent needles which easily effloresce. The *sodium salt*, $\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}^-\text{Na} + \text{H}_2\text{O}$, crystallises on cooling from hot solutions in large flat prisms, which effloresce on exposure to the air, and when left in the mother-liquor quickly change to thick crystals resembling gypsum, which do not effloresce, although they still retain 1 mol. water. It is less soluble than the potassium salt. The *barium salt*, $(\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}^-)^2\text{Ba} + 1\frac{1}{2}\text{H}_2\text{O}$, forms small faintly reddish prisms moderately soluble in hot, slightly in cold water. The *calcium salt*, $(\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}^-)^2\text{Ca}$, crystallises in concentric groups of needles, moderately soluble in water; the *lead salt*, $(\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}^-)^2\text{Pb} + \text{H}_2\text{O}$, in tufts of small very flat prisms, somewhat sparingly soluble.

The *chloride*, $\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}^-\text{Cl}$, appears to be formed by heating the potassium salts with phosphorus pentachloride, but the residue left after washing with water consists merely of reproduced dibromorthamidobenzenesulphonic acid.

This acid has the constitution represented by the first of the following formulæ; for when treated with bromine it exchanges the group SO^-H for Br, and is converted into the tribromaniline represented by the second formula (ordinary tribromaniline); hence also the dibromobenzenesulphonic acid formed by substitution of H for NH_2 in this amidated acid must have the symmetrical constitution represented by the third formula:

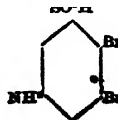
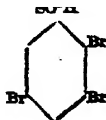
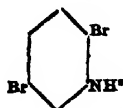


Dibromometamidobenzenesulphonic acid, $\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}_3\text{H}$.—When 2 mols. bromine are added to a hot concentrated solution of the metamid-acid, a very violent action takes place, the colour of the bromine disappears immediately, and the dibrominated acid ultimately settles down as a sandy precipitate, the supernatant liquid still retaining a considerable quantity of it, which may be obtained by evaporation.

Purified by recrystallisation from hot water, it forms small white anhydrous needles, which do not melt when heated, and decompose only at a very high temperature. It is but sparingly soluble in hot, still less in cold water, insoluble in alcohol and ether, somewhat freely soluble in the original liquid still containing hydrobromic acid.

The *potassium salt*, $\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}_3^-\text{K} + \text{H}_2\text{O}$, forms easily soluble nacreous laminae. The *barium salt*, $(\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}_3^-)^2\text{Ba} + 6\text{H}_2\text{O}$, forms transparent colourless monoclinic prisms often several inches long, easily soluble in water, efflorescing and falling to powder on exposure to the air. The *lead salt*, $(\text{C}_6\text{H}_2\text{Br}_2\text{NH}_2\text{SO}_3^-)^2\text{Pb}$, crystallises in moderately soluble, thin, nacreous, anhydrous laminae (Berndsen & Limpricht, *Liebigs Annalen*, clxxvii. 84; Beckurts, *ibid.* clxxxi. 213).

An acid apparently identical with the preceding is obtained (together with a tribromamido-acid) by the action of tin and hydrochloric acid on the nitrotribromobenzenesulphonic acid represented by the formula $\text{C}_6\text{H}_2\text{Br}_3\text{NO}_2\text{SO}_3\text{H}$ (p. 247). This dibromamido-acid crystallises in small white or faintly reddish anhydrous needles, which are decomposed by heat without previous fusion, are but slightly soluble in water, and nearly insoluble in alcohol. Heated to 120° with hydriodic acid and amorphous phosphorus, it is converted into *metamidobenzenesulphonic acid*. Its *potassium salt* forms radiate groups of microscopic needles containing $1\frac{1}{2}\text{H}_2\text{O}$; the *barium salt* long efflorescent needles containing $6\text{H}_2\text{O}$; the *calcium salt*, microscopic, very soluble needles, with $2\text{H}_2\text{O}$; the *lead salt* (anhydrous) nodular groups of microscopic laminae. All these salts are easily soluble in water. The *diazo*-compound, obtained in small quantity by the action of nitrous acid on the dibromamido-acid, is converted by the action of concentrated hydrobromic acid into a tribromobenzenesulphonic acid, which is most probably constituted according to the formula $\text{C}_6\text{H}_2\text{Br}_3\text{SO}_3\text{H}$ (p. 240), whence it follows that the amidodibromobenzenesulphonic acid may be represented by either the first or the third of the following formulæ, the tribrominated acid being represented by the second:—

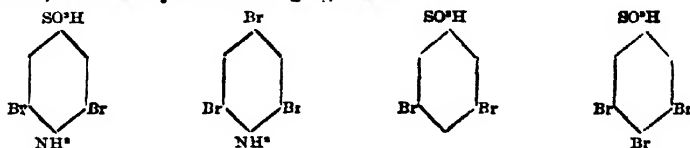


(Kauts, *Liebigs Annalen*, clxxvi. 301).

(3). *Dibromoparamidobenzenesulphonic acid*, $C^6H^3SO^3H.Br.NH^2.Br.H$ (Lenz, *Deut. Chem. Ges. Ber.* viii. 1086; *Liebig's Annalen*, clxxi. 24).—This acid, obtained by the action of bromine on sulphanilic acid, crystallises in transparent obtuse prisms which give off their water of crystallisation on exposure to the air. Its

barium and lead salts are sparingly soluble. The *diazo-compound*, $C^6H^3Br^2 \begin{matrix} N=N \\ \diagup \quad \diagdown \\ SO^3H \end{matrix}$ formed by passing nitrous acid into the alcoholic solution of the acid, separates in microscopic, square, colourless, or yellowish plates, which become darker in the air and have a bitter taste.

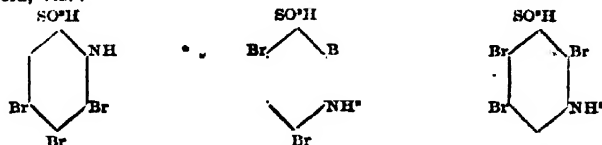
This dibromamido-acid is converted by treatment with excess of bromine into ordinary tribromaniline, 1 : 2 : 4 : 6 (NH^2 in 1), and by exchange of NH^2 for H (action of nitrous ether) into symmetric dibromobenzenesulphonic acid; and the diazo-compound, heated with hydrobromic acid, yields (1 : 3 : 4 : 5) tribromobenzenesulphonic acid. These transformations demonstrate the constitution of the dibromamido-acid, as shown by the following figures:—



(4). *Amidoparadibromobenzenesulphonic acid*, $SO^3H : Br : Br : NH^2 = 1 : 2 : 5 : x$, the position of the NH^2 not being yet determined. The nitro-acid obtained by nitration of *paradibromobenzenesulphonic acid* yields, by reduction with tin and hot hydrochloric acid, an amidated acid which crystallises from strong solutions in delicate white needles containing $0.5H^2O$, which dry up in the filter to a felted mass; from dilute solutions it separates in prisms having a faint violet colour. It decomposes when heated above 150° without previous fusion, dissolves sparingly in alcohol and in cold water, and not readily even in hot water. Its salts are very soluble. The *potassium salt*, $C^6H^3Br^2(NH^2)SO^3K$, separates slowly from concentrated solutions in large anhydrous monoclinic tablets. The *barium salt*, $[C^6H^3Br^2(NH^2)SO^3]^2Ba + H^2O$, crystallises from concentrated solution in groups of transparent prisms, which turn reddish in the air and dissolve easily in alcohol. The *lead salt*, $[C^6H^3Br^2(NH^2)SO^3]^2Pb + 8H^2O(?)$, forms plumose groups of small white needles soon turning brown, or light-brown prisms.

The *diazo-compound* of this acid crystallises in light-yellow prisms which detonate when heated. It dissolves easily in water, with moderate facility in alcohol, and is precipitated from the alcoholic solution by ether. The aqueous solution decomposes quickly, the alcoholic solution more slowly. By the action of concentrated hydrobromic acid this diazo-compound is converted into a tribromobenzenesulphonic acid, the constitution of which has not yet been determined (Born, *Liebig's Annalen*, clxxvi. 362).

Tribromamidobenzenesulphonic Acids, $C^6HBr^3(NH^2)SO^3H$. Of these acids three are known, one derived from *ortho*- and two from *meta*-amidobenzenesulphonic acid, viz.:—



1. *Tribromorthoamidobenzenesulphonic acid* is obtained by the action of tin and hydrochloric acid on the corresponding nitro-acid, which is formed by nitration of tribromobenzenesulphonic acid, $C^6SO^3H.NH^2.Br.Br.Br.H$. It crystallises in tufts of colourless or slightly reddish, slender, flexible needles, which, under the microscope, exhibit pointed summits or oblique end-faces. It dissolves easily in water and in alcohol of 95 p. c., and its concentrated aqueous solution gives precipitates with barium chloride and lead acetate. It easily blackens when heated. Its barium salt, $[C^6HBr^3(NH^2)SO^3]^2Ba + 1\frac{1}{2}H^2O$, dissolves sparingly in cold, easily in hot water, and crystallises on cooling in colourless laminae, becoming yellow after repeated crystallisation.

The *diazo-compound* of this acid separates from a well-cooled concentrated aqueous

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solution as a colourless powder made up of short microscopic prisms. From alcoholic solution it separates in tufts of slender microscopic needles. It appears to be permanent in the dry state, and explodes when heated, but not by percussion. It is moderately soluble in water and in alcohol, and decomposes slowly in the alcoholic, quickly in the aqueous solution at summer temperature. Strong hydrobromic acid decomposes it on prolonged boiling, forming consecutive tetrabromobenzenesulphonic acid (1 : 2 : 3 : 4 : 5) (Lenz, *Liebig's Annalen*, clxxxi. 43).

2. *Tribromometamidobenzenesulphonic acid* (with symmetrical bromine-atoms), $\text{C}^6\text{H}_3\text{Br}_3\text{NH}^2\text{Br} \cdot \text{H} \cdot \text{Br}$, is formed by the action of tin and hydrochloric acid on a well-cooled solution of the corresponding nitro-acid. It is usually accompanied by a small quantity of a dibromamido-acid, which, at higher temperatures, forms the chief product, especially if the action be prolonged.

This tribrominated acid crystallises in long slender needles having a silky lustre, moderately soluble in cold, more soluble in warm water, slightly soluble in alcohol. It has a slightly astringent taste, blackens when heated above 200° in a test-tube, and burns on platinum foil without previous fusion. The concentrated solution is precipitated by potassium carbonate and lead acetate, but not by chloride of barium or calcium.

The corresponding *diazo-compound*, which crystallises in microscopic, rhombic, nearly square plates, is converted by boiling hydrobromic acid into a consecutive tetrabromobenzenesulphonic acid, $\text{C}^6\text{H}_2\text{Br}_4\text{SO}^3\text{H} \cdot \text{Br} \cdot \text{Br} \cdot \text{H} \cdot \text{Br}$ (Reinle, *Liebig's Annalen*, clxxxi. 281).

3. *Tribromometamidobenzenesulphonic acid*, $\text{C}^6\text{H}_3\text{Br}_3\text{NH}^2 \cdot \text{H} \cdot \text{Br} \cdot \text{Br}$ (with unsymmetrical bromine-atoms), is formed, together with a dibromamido acid (p. 232), by the action of bromine on *m*-amidobenzenesulphonic acid. The two acids may be separated by recrystallisation from hot water, or, better, from boiling alcohol, in which the tribrominated acid is easily soluble, whereas the dibrominated acid is nearly insoluble.

The tribrominated acid crystallises in slender colourless needles which dissolve easily in hot, much less easily in cold water and alcohol, and carbonise when heated, without previous fusion. Bromine added to the hot aqueous solution throws down tetrabromoquinone.

The *potassium salt*, $\text{C}^6\text{H}_3\text{Br}_3(\text{NH}^2)\text{SO}^3\text{K} + \text{H}^2\text{O}$, forms thin nacreous laminae easily soluble in hot, sparingly in cold water. The *barium salt*, $[\text{C}^6\text{H}_3\text{Br}_3(\text{NH}^2)\text{SO}^3]^2\text{Ba} + 9\text{H}^2\text{O}$, forms small shining rhombic plates, easily soluble in hot, sparingly in cold water.

The *diazo-compound*, formed by passing a rapid current of nitrogen trioxide into a strong alcoholic solution of the acid, crystallises in small yellow rhombic tables which burn vividly when heated on platinum foil. It dissolves with red colour in hot water, nitrogen being evolved; and is decomposed by boiling alcohol under pressure. Hydrobromic and hydriodic acids dissolve it easily (Beckurts, *Liebig's Annalen*, clxxxi. 215).



by reducing the corresponding nitro-acid with tin and hydrochloric acid, crystallises in slender microscopic needles, easily soluble in hot, less soluble in cold water and alcohol, and charring without previous fusion when heated on platinum foil. It is not converted into bromanil either by bromine or by chromic acid.

The *potassium salt*, $\text{C}^6\text{H}_2\text{Br}_4(\text{NH}^2)\text{SO}^3\text{K} + 1\frac{1}{2}\text{H}^2\text{O}$, forms nacreous prisms slightly soluble in water. The *barium salt*, $[\text{C}^6\text{H}_2\text{Br}_4(\text{NH}^2)\text{SO}^3]^2\text{Ba} + \text{H}^2\text{O}$, crystallises in laminae which are sparingly soluble in water and separate slowly again from the solution. The *calcium salt*, $[\text{C}^6\text{H}_2\text{Br}_4(\text{NH}^2)\text{SO}^3]\text{Ca} + 7\text{H}^2\text{O}$, separates on cooling from the hot aqueous solution in laminae having a satiny lustre, easily soluble in hot, sparingly in cold water.

The *diazo-compound*, $\text{C}^6\text{H}_2\text{Br}_4\text{N}^2\text{SO}^3$, obtained by passing a rapid current of nitrogen trioxide into an alcoholic solution of the amido-acid, forms microscopic rhombic tables, which explode feebly when heated. It dissolves in hot water with decomposition, but is not decomposed by boiling with alcohol. Hot hydrobromic acid dissolves it with turbid evolution of nitrogen, forming pentabromobenzenesulphonic acid, $\text{C}^6\text{H}_2\text{Br}_5\text{SO}^3\text{H}$ (Beckurts, *Liebig's Annalen*, clxxxi. 225).

Methylamidobenzenesulphonic or Methylanilinesulphonic Acid,
 $\text{C}^6\text{H}_5\text{NH}(\text{OH})\text{SO}^3\text{H}$ (G. A. Smyth, *Deut. Chem. Ges. Ber.* 1874, 1237). This acid is

formed, together with methenedisulphonic (methionie) acid, $\text{CH}_2(\text{SO}^3\text{H})_2$, by heating methylacetanilide with sulphuric acid to 140° – 150° as long as acetic acid is thereby evolved. The liquid, diluted with water, neutralised with barium carbonate, and filtered while hot, deposits, on cooling, a white crystalline powder consisting of the barium salt of methenedisulphonic acid, $\text{CH}_2(\text{SO}^3\text{H})_2$, formed by the action of the sulphuric acid on the acetic acid; and the mother-liquor contains the barium salt of methylaniline-sulphonic acid, which, when freed from adhering red colouring matter by repeated crystallisation, with the aid of animal charcoal, forms white laminae having the composition $(\text{C}^6\text{H}^4\cdot\text{NHCH}^3\cdot\text{SO}^3)^2\text{Ba} + \text{H}^2\text{O}$. The free acid forms anhydrous crystals which decompose at 182° without previous fusion. With bases it forms well-crystallised, extremely soluble salts. The lead-salt separates from aqueous solution in microscopic crystals.

Dimethylanilinesulphonic acid, $\text{C}^6\text{H}^4\langle\begin{smallmatrix} \text{N}(\text{OH}^3) \\ \text{SO}^3\text{H} \end{smallmatrix}\rangle$, is obtained by heating dimethylaniline to 180° – 190° with rather more than the equivalent quantity of sulphuric acid, till a sample almost ceases to give a precipitate with caustic soda. The solution, which does not deposit crystals even on strong concentration, is neutralised with barium carbonate, and the acid is separated from the resulting barium salt in the usual way. It melts with decomposition at 149° – 150° . It is not altered by fuming sulphuric acid. With the alkalis and alkaline earths, and with some of the heavy metals, it forms well-crystallised salts, all of which contain water, and, excepting the ammonium salt, are all easily soluble in water, sparingly in alcohol. The copper and silver salts are easily reducible (Smyth).

Ethylanilinesulphonic Acid, $\text{C}^6\text{H}^4\langle\begin{smallmatrix} \text{NH}(\text{C}^2\text{H}^5) \\ \text{SO}^3\text{H} \end{smallmatrix}\rangle$, is formed by heating ethylaniline with sulphuric acid to 190° for several days. Its purification is difficult and can be effected only by repeatedly precipitating the barium salt with alcohol and ether, this salt being thereby obtained, first as a red gummy mass, afterwards as a light red powder having the composition $(\text{C}^6\text{H}^4\cdot\text{NHCH}^2\text{H}^5\cdot\text{SO}^3)^2\text{Ba} + 2\text{H}^2\text{O}$. The acid itself is anhydrous and decomposes at about 250° (Smyth).

Armstrong (*Deut. Chem. Ges. Ber.* vi. 663), by heating ethylaniline with sulphuric acid, obtained, not the acid just described, but only amidobenzenesulphonic (sulphanilic) acid. Smyth, however, finds that when the ethylaniline used has been previously purified from aniline by treating it with sulphuric acid at ordinary temperatures till aniline sulphate no longer separates from it, and it gives scarcely any coloration with chloride of lime, it yields no more than traces of sulphanilic acid when treated as above, whereas somewhat larger quantities of sulphanilic acid are obtained from ethylaniline which has been purified merely by fractional distillation. It may be concluded, therefore, that Armstrong's result was due to the presence of aniline in the ethylaniline employed.

Diethylanilinesulphonic acid, $\text{C}^6\text{H}^4\langle\begin{smallmatrix} \text{N}(\text{C}^2\text{H}^5)_2 \\ \text{SO}^3\text{H} \end{smallmatrix}\rangle$, is obtained by prolonged heating of ethylaniline with sulphuric acid to 200° – 210° , and is also very difficult to purify. It was obtained as a reddish anhydrous powder, not decomposing at 250° . The barium salt has the composition $[\text{C}^6\text{H}^4\cdot\text{N}(\text{C}^2\text{H}^5)_2\cdot\text{SO}^3]^2\text{Ba} + 2\text{H}^2\text{O}$. The salts of both these ethylated acids are crystallisable, but not well defined; the silver salts cannot be prepared, as they are too easily reduced (Smyth).

Bromobenzenesulphonic Acids. The three modifications of the monobrominated acid, $\text{C}^6\text{H}^4\text{Br}\cdot\text{SO}^3\text{H}$, are obtained from the corresponding amidated acids by treating the latter with nitrous acid, and heating the resulting diazobenzenesulphonic acid with hydrobromic acid (Lamprecht, *Deut. Chem. Ges. Ber.* viii. 456, 1065; *Liebig's Annalen*, clxxvii. 92, 101).

Parabromobenzenesulphonic acid, $\text{C}^6\text{H}_3\text{Br}\cdot\text{H}\cdot\text{SO}^3\text{H}\cdot\text{H}^2$, prepared in this manner from sulphanilic acid, is identical with the acid obtained by the action of fuming sulphuric acid on bromobenzene, or of bromine on benzenesulphonic acid (2nd Suppl. 153). According to Nölting (*Deut. Chem. Ges. Ber.* viii. 352) the same modification is produced by passing the vapour of sulphuric anhydride through bromobenzene. Armstrong (*Zeitschr. f. Chem.* [2], vii. 321), by treating bromobenzene with sulphuric hydroxychloride, 80°ClOH , obtained a bromobenzenesulphonic acid, whose barium salt crystallised with 3 mols. water; according to Nölting a. Wrzeszinski, on the other hand, the acid thus prepared yields a barium salt which crystallises from hot solutions in anhydrous laminae; and by slow evaporation at ordinary temperatures in nodules containing $2\text{H}^2\text{O}$, like the barium salt of the ordinary acid prepared by treating bromobenzene with sulphuric acid.

The following parabromobenzenesulphonates are described by C. Goslich (*Deut. Chem. Ges. Ber.* viii. 352; *Liebig's Annalen*, clxxx. 93):—

Free acid, $\text{C}_6\text{H}_4\text{Br}_2\text{SO}_3\text{H}$. Deliquescent needles.

Ammonium salt, $\text{C}_6\text{H}_4\text{Br}_2\text{SO}_3\text{NH}_4$. Large transparent prisms.

Potassium salt, $\text{C}_6\text{H}_4\text{Br}_2\text{SO}_3\text{K}$. Small white needles.

Barium salt, $(\text{C}_6\text{H}_4\text{Br}_2\text{SO}_3)_2\text{Ba}$. Large glistening plates.

Calcium salt, $(\text{C}_6\text{H}_4\text{Br}_2\text{SO}_3)_2\text{Ca} + 2\text{H}_2\text{O}$. Warty tufts.

Lead salt, $(\text{C}_6\text{H}_4\text{Br}_2\text{SO}_3)_2\text{Pb} + 2\text{H}_2\text{O}$. Warty plates.

According to Nörling, the lead salt crystallises from a hot concentrated solution in hemispherical anhydrous masses; from dilute solutions in rhombic plates containing 2 mols. water.

The chloride, $(\text{C}_6\text{H}_4\text{Br}_2\text{SO}_2\text{Cl})$, crystallises from ether in large transparent crystals, resembling axinite, and melting at 75° .

The amide, $\text{C}_6\text{H}_4\text{Br}_2\text{SO}_2\text{NH}_2$, forms needles, melting at 160° .

The potassium salt, distilled with dry *potassium ferrocyanide*, yields a dicyanobenzene, $\text{C}_6\text{H}_4(\text{CN})_2$, which crystallises from alcohol in beautiful shining needles, melting at 215° , and when heated to 150° in sealed tubes with hydrochloric acid, is completely resolved into ammonia and terephthalic acid (Limpricht).

Metabromobenzenesulphonic acid, $\text{C}_6\text{H}_3\text{Br.H.SO}_3\text{H.H}^+$ (Berndsen, *Liebig's Annalen*, clxxvii. 92).—The diazo-compound of metamidobenzenesulphonic acid mixed with hydrobromic acid and evaporated yields a mixture of metabromobenzenesulphonic and phenolsulphonic acids, which, when neutralised with barium carbonate, yields crystals of barium metabromobenzenesulphonate and a non-crystallisable mother-liquor containing the phenolsulphonate.

According to A. Thomas (*ibid.* clxxxvi. 123), this amido-acid is more easily prepared (as first proposed by Nörling) by the action of bromine on silver benzenesulphonate. Pure benzenesulphonic acid is neutralised with silver carbonate, and bromine is added to the still warm filtrate as long as silver bromide is thereby precipitated. On evaporating the filtered liquid over a water-bath till it no longer smells of bromine, then neutralising with barium carbonate and evaporating the filtrate, barium metabromobenzenesulphonate separates out in hard crusts, easily purified by recrystallisation, with aid of animal charcoal.

The following metabromobenzenesulphonates have been prepared:—

Ammonium salt: very easily soluble, warty crystals.

Potassium salt, $\text{C}_6\text{H}_3\text{Br.SO}_3\text{K} + \text{H}_2\text{O}$. Small nodules.

Barium salt, $(\text{C}_6\text{H}_3\text{Br.SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ and $2\frac{1}{2}\text{H}_2\text{O}$. Small, snow-white nodules.

Lead salt, $(\text{C}_6\text{H}_3\text{Br.SO}_3)_2\text{Pb} + 2\text{H}_2\text{O}$. Resembles the barium salt.

The chloride is an oily liquid. The amide, $\text{C}_6\text{H}_3\text{Br.SO}_2\text{NH}_2$, crystallises from hot water in slender needles or shining laminae; from alcohol in thicker prisms. Melts at 153° – 154° .

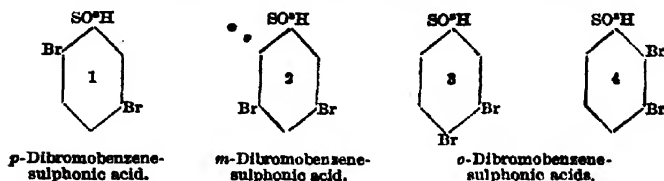
Metabromobenzenesulphonic acid, fused with potash, yields resorcin. Its potassium salt, distilled with dry potassium ferrocyanide, yields a dicyanobenzene which crystallises in nodular groups of small needles melting at 147° – 148° , and converted by heating with hydrochloric acid into isophthalic acid (Berndsen).

Orthobromobenzenesulphonic acid, $\text{C}_6\text{H}_4\text{Br.SO}_3\text{H.H}^+$ (Berndsen & Limpricht *Liebig's Annalen*, clxxvii. 101; Bahlmann, *ibid.* clxxxi. 203; clxxxvi. 315).—This acid is obtained by evaporating the diazo-compound obtained from orthamidobenzenesulphonic acid with hydrobromic acid (b. p. 126°), and may be purified by converting it into a potassium salt, treating this salt with phosphorus pentachloride, crystallising the resulting sulphochloride, and finally decomposing it with water at 140° – 160° . The free acid crystallises from concentrated solutions in long brown deliquescent needles which dissolve freely in alcohol. Its salts are easily soluble in water. The *ammonium salt*, $\text{C}_6\text{H}_4\text{Br.SO}_3(\text{NH}_4)$, forms white tabular crystals. The *potassium salt*, $\text{C}_6\text{H}_4\text{Br.SO}_3\text{K} + \text{H}_2\text{O}$, crystallises in four-sided tablets. The *barium salt*, $(\text{C}_6\text{H}_4\text{Br.SO}_3)_2\text{Ba}$, forms small prisms or small needles with various proportions of water. The *calcium salt*, $(\text{C}_6\text{H}_4\text{Br.SO}_3)_2\text{Ca} + 2\text{H}_2\text{O}$, forms small white tablets. The *lead salt*, $(\text{C}_6\text{H}_4\text{Br.SO}_3)_2\text{Pb} + 3\text{H}_2\text{O}$, crystallises in transparent rhombic prisms. The *silver salt*, $\text{C}_6\text{H}_4\text{Br.SO}_3\text{Ag}$, forms white pearly laminae, which decompose slowly on exposure to light.

The chloride, $\text{C}_6\text{H}_4\text{Br.SO}_2\text{Cl}$, solidifies at low temperatures, and crystallises from ether in tufts of pointed prisms melting at 51° .

The amide, $\text{C}_6\text{H}_4\text{Br.SO}_2\text{NH}_2$, forms long white brittle needles, sparingly soluble in water and melting at 186° .

Dibromobenzenesulphonic Acid, $\text{C}_6\text{H}_2\text{Br}_2\text{SO}_3\text{H}$. Of the six possible modifications of this acid, five have been obtained, and the structure of four of these has been determined, two being unsymmetrical, one symmetrical, and one consequent on



The two unsymmetrical modifications, (1) and (3) are obtained simultaneously by the action of bromine on the silver salt of metabromobenzenesulphonic acid. To prepare them, bromine is added to silver metabromobenzenesulphonate as long as silver bromide separates, and the filtered liquid is treated with barium carbonate and evaporated. A mixture of barium salts is thereby obtained, consisting chiefly of monobromobenzenesulphonate mixed with *paradibromobenzenesulphonate* (1 : 2 : 6) and a small quantity of *orthobromobenzenesulphonate* (1 : 3 : 4). The salts of the two dibrominated acids are deposited in comparatively large druses on the hard crystals of the monobrominated salt; they may be obtained tolerably pure by levigation with the mother-liquor, and further purified by recrystallisation. To separate the corresponding acids one from the other, the barium salts are converted into potassium salts, and from these the chlorides $\text{C}^6\text{H}^3\text{Br}^2\text{SO}^{\text{H}}\text{Cl}$ are prepared by the action of phosphorus pentachloride. The ethereal solution of these mixed chlorides, when left to evaporate, first deposits compact crystals of *paradibromobenzenesulphochloride* (m. p. 71°), leaving an oily mixture of this compound with the *ortho*-modification. For further separation, these chlorides are converted by the action of ammonia into amides, $\text{C}^6\text{H}^3\text{Br}^2\text{SO}^{\text{H}}\text{NH}^2$, and these are separated by repeated crystallisation from water and dilute alcohol, *paradibromobenzenesulphamide* (m. p. 193°) crystallising out first, and afterwards a mixture of amides melting at about 150° , from which, by repeated recrystallisation, *orthodibromobenzenesulphamide* may be separated, melting at 170° – 171° . The amides heated to 170° in sealed tubes with hydrochloric acid yield the corresponding acids.

1. *Paradibromobenzenesulphonic acid*, $\text{C}^6\text{SO}^{\text{H}}\text{H}.\text{Br}.\text{H}.\text{H}.\text{Br}.\text{H}$ (Thomas, *Liebig's Annalen*, cxxxvi. 129; Limpricht, *ibid.* 139; Bahlmann, *ibid.* 312, 321; Borns, *ibid.* cxxxvii. 353).—This acid is produced: 1. By the action of fuming sulphuric acid on *paradibromobenzene*. This is the process by which it was first prepared (*2nd Suppl.* 253). To obtain a pure product, crystallised *paradibromobenzene* (m. p. 89°) is mixed with twice its volume of fuming sulphuric acid in a loosely stoppered flask, and the mixture is left for eight to fourteen days on a sand-bath at a temperature not exceeding 100° ; the contents of the flask are then poured into water; the solution is filtered from unattacked *dibromobenzene*; and the latter, after washing and drying, is treated with fuming sulphuric acid as before. The strongly acid solution thus obtained often deposits, after a while, crystals of the *dibromobenzenesulphonic acid*, which, after being pressed and recrystallised, are quite pure. The remaining solution is neutralised with lime, strained, evaporated, and filtered from gypsum; the filtrate is treated with barium chloride; and the barium *dibromobenzenesulphonate* thereby precipitated is purified by recrystallisation and decomposed by sulphuric acid (Borns).

2. Together with *orthodibromobenzenesulphonic acid*, by the action of bromine on the silver salt of metabromobenzenesulphonic acid. The mode of separating the two dibrominated acids thus produced, by conversion into the chlorides and amides, has just been explained. The *para*-acid is obtained by heating the chloride melting at 71° , with water to 170° in sealed tubes, and evaporating the resulting solution to a syrupy consistence (Limpricht).

3. By the action of concentrated hydrobromic acid on the diazo-compound of metabromorthamidobenzenesulphonic acid, $\text{C}^6\text{SO}^{\text{H}}\text{H}.\text{NH}^2.\text{H}.\text{H}.\text{Br}.\text{H}$ (Thomas & Bahlmann), or of orthobromometamidobenzenesulphonic acid, $\text{C}^6\text{SO}^{\text{H}}\text{H}.\text{Br}.\text{H}.\text{H}.\text{NH}^2.\text{H}$ (Bahlmann).

Paradibromobenzenesulphonic acid crystallises from its aqueous solution by evaporation over sulphuric acid, in fine, limpid, non-efflorescent prisms containing 3 mols. of crystallisation-water, easily soluble in water, less soluble in alcohol, nearly insoluble in ether. The crystals melt at about 98° , but the exact melting point is difficult to determine, since at this temperature water is given off, and then the melting point rises. On prolonged heating to 98° , or a few degrees above, the acid solidifies to a light brown shining crystalline mass, which, in contact with moist air, takes up water again, and then melts at 98° . Of the 3 mols. crystallisation-water, two are given off at 100° , the remainder at 130° . The anhydrous acid melts at 128° .

The following salts are described by Borns: $\text{C}^6\text{H}^3\text{Br}^2\text{SO}^{\text{H}}(\text{NH}^2)$, anhydrous.

Plumose groups of delicate needles very soluble in water and in alcohol. On heating the salt with alcoholic ammonia to 200°–210° for several hours, a small quantity of bromine is given off.

$C^6H^4Br^2.SO^3K + H^2O$. Separates by slow crystallisation in long flat prisms; otherwise in slender needles. Dissolves easily in water; effloresces slowly in the air, and crumbles to powder when dried at a higher temperature.

$C^6H^4Br^2.SO^3Na + 1.5H^2O$. Slender needles having a satiny lustre.

$C^6H^4Br^2.SO^3Ag + 1.5H^2O$. White prisms, or from dilute solutions, long pointed needles, not altered in the dry state by exposure to the air. Dissolves in about 60 parts of water at 9°.

$(C^6H^4Br^2.SO^3)^2Ba + xH^2O$. This salt crystallises under different circumstances with various proportions of water, from 1 to 7 mols.; but by repeated crystallisation these different hydrates are for the most part converted into the monohydrate, which crystallises in nacreous, non-efflorescent, rhombic laminæ, and gives off the whole of its water at 140°. Limpricht obtained from very dilute solutions needles containing $1\frac{1}{2}H^2O$; from stronger solutions laminæ with $1H^2O$. Concentrically grouped needles with $2H^2O$ have been obtained by Hübner a. Williams (2nd Suppl. 154), by Bahlmann and by Borns. Crystals containing 3 mols. water were observed by Bahlmann, and Thomas obtained crystals containing $1\frac{1}{2}$ to 5 mols. water. The barium salt which Borns obtained from the dibromobenzenesulphonic acid prepared from the diazo-compound of amidobromobenzenesulphonic acid, contained 5 mols. water: they were light brown prisms and hemispherical groups of long white efflorescent needles, which crumbled to a white powder when dried. Finally, Limpricht found $7H^2O$ in a salt which separated from a dilute solution after long standing. This hydrate formed large transparent rhombic prisms, apparently made up of flat laminæ; they were very brittle, easily breaking at right angles to their axis when touched.

$(C^6H^4Br^2.SO^3)^2Ca + 10H^2O$. Separates from concentrated solutions in very long pointed needles; from more dilute solutions in laminæ, easily soluble in water and alcohol. The crystals effloresce very quickly, crumbling completely to powder after a few days exposure to the air. Wölz found $9H^2O$ in this salt. Hübner a. Williams found $4H^2O$.

$(C^6H^4Br^2.SO^3)^2Pb + 3H^2O$. Groups of faintly yellowish laminæ, which effloresce slightly on long exposure to the air. It is somewhat sparingly soluble in water, but very slow in separating from the solution. Borns also obtained a lead salt with $4H^2O$, which crystallised in flat, limpid, efflorescent needles.

The chloride, $C^6H^4Br^2.SO^3Cl$, crystallises from ether in well-defined monoclinic (?) tables or in nacreous laminæ. Melts at 71°–72°.

The amide, $C^6H^4Br^2.SO^3NH^2$, crystallises in long slender needles which dissolve very sparingly in cold water and melt at 193°.

(2.) *Metadibromobenzenesulphonic acid* (1 : 3 : 5) is prepared from dibromoparamidobenzenesulphonic (dibromosulphanilic) acid, $C^6.SO^3H.H.Br.NH^2.Br.H$, and from dibromorthamidobenzenesulphonic acid, $C^6.SO^3H.NH^2.Br.H.Br.H$. (pp. 231, 232), by substitution of H for NH^2 (action of nitrous ether). It forms a crystalline, easily soluble mass. Its salts crystallise well, and are for the most part sparingly soluble in water. The following have been examined.

$C^6H^4Br^2.SO^3(NH^2)$. Anhydrous glistening colourless crystals.

$C^6H^4Br^2.SO^3K$. Large brownish, anhydrous crystals.

$(C^6H^4Br^2.SO^3)^2Ba + 3\frac{1}{2}H^2O$. Long yellow needles.

$(C^6H^4Br^2.SO^3)^2Ca + 3\frac{1}{2}H^2O$. Small hexagonal plates.

$(C^6H^4Br^2.SO^3)^2Pb + 1\frac{1}{2}H^2O$. White scales composed of microscopic needles.

The chloride, $C^6H^4Br^2.SO^3Cl$, forms large well-defined crystals melting at 57.5°.

The amide, $C^6H^4Br^2.SO^3NH^2$, forms dazzling white scales, melting at 203° (Limpricht, *Deut. Chem. Ges. Ber.* viii. 1066; Lenz, *Liebigs Annalen*, clxxi. 23; Berendsen a. Limpricht, *ibid.* 193).

Orthodibromobenzenesulphonic acids. (3.) The modification, $C^6.SO^3H.H.Br.Br.H$, is obtained as above, together with the para-acid, by the action of bromine on the silver salt of *metabromobenzenesulphonic acid*, and more abundantly, without the formation of any other modification, by the action of bromine on the silver salt of *parabromobenzenesulphonic acid*. Its formation from these two modifications of monobromobenzenesulphonic acid establishes its constitution (Limpricht, *Liebigs Annalen*, clxxvi. 145; Göslich, *ibid.* 148).

By converting the silver salt into a barium salt, decomposing the latter with sulphuric acid, and leaving the filtrate to evaporate over sulphuric acid, the free acid is obtained in felted groups of white slender needles, containing $C^6H^4Br^2.SO^3H + 3H^2O$, and melting at 57°–58°. The dehydrated acid obtained by heating these crystals to 120° is so hygroscopic that its melting point cannot be determined.

The following salts have been prepared :—

$C^6H^4Br^2SO^3K$. White indistinct crystals, extremely soluble in water, less soluble in alcohol, and separating therefrom without water of crystallisation.

$C^6H^4Br^2SO^3(NH^4)$. White felted, anhydrous, very soluble needles.

$(C^6H^4Br^2SO^3)^2Ba$. Crystallises mostly in thin flat tablets containing $2H^2O$, sometimes in long shining needles with $3H^2O$. The salt (reckoned as anhydrous) dissolves in about 25 pts. of water at 16° .

$(C^6H^4Br^2SO^3)^2Ca$ (anhydrous). Thick shining laminæ, much more soluble than the barium or lead salt.

$(C^6H^4Br^2SO^3)^2Pb + 2H^2O$. Thin white laminæ resembling those of the barium salt; soluble in 37 parts of water at 8° (reckoned as anhydrous).

$C^6H^4Br^2SO^3Ag$. Long, narrow, lanceolate, acuminate, nacreous needles, sparingly soluble in water.

The chloride, $C^6H^4Br^2SO^3Cl$, is obtained by heating the potassium salt to 120° – 130° in a sealed tube with 1 mol. PCl^3 and a small quantity of $POCl^3$, and separates from ether as an oil which remains fluid for a long time, but solidifies in a freezing mixture, forming tufts of white needles which melt at 31° .

The amide, $C^6H^4Br^2SO^3NH^2$, forms white felted needles, very slightly soluble in cold water, more freely in dilute alcohol, melting at 170° (Goslich).

(4.) The consecutive modification, $C^6SO^3H.Br.Br.H^2$, is formed by passing nitrous acid vapour through concentrated hydrobromic acid containing in suspension the corresponding diamidobenzenesulphonic acid (p. 229); heating the liquid after awhile to the boiling point, again passing nitrous acid through it, again heating, and so on, as long as nitrogen continues to escape on heating. The liquid is then evaporated over the water-bath to expel the excess of hydrobromic acid, and the residue is dissolved in water and neutralised with barium carbonate. A dark-brown barium salt is thereby obtained, which may be decolorised by alternately precipitating the barium with sulphuric acid, and neutralising with barium carbonate, till the salt retains only a faint reddish tint, and removing this by four hours' boiling with animal charcoal.

The free acid separated from this salt by sulphuric acid remains, on evaporating its solution, in rather large, transparent, colourless prisms, which deliquesce very quickly on exposure to the air. Its salts are, for the most part, sparingly soluble.

$C^6H^4Br^2SO^3K$ crystallises in transparent, colourless, anhydrous laminæ having a mother of pearl lustre, and slightly soluble in water.

$(C^6H^4Br^2SO^3)^2Ba + 3H^2O$ crystallises from very dilute solutions in tufts of white curved needles; hot concentrated solutions solidify on cooling from separation of slender needles; sometimes also the salt separates in small white nodules. It is very slightly soluble in water.

$(C^6H^4Br^2SO^3)^2Ca + 2H^2O$ separates on cooling from a hot concentrated solution in white granulo-crystalline forms, moderately soluble in water.

$(C^6H^4Br^2SO^3)^2Pb + 3H^2O$. Stillate groups of white needles, crumbling to scales in contact with the air; rather sparingly soluble in water.

The chloride, $C^6H^4Br^2SO^3Cl$, after repeated crystallisation from ether, forms white prismatic crystals melting at 127° . The amide, $C^6H^4Br^2SO^3NH^2$, crystallises from alcohol in small white needles, slightly soluble in water, easily in alcohol, melting and turning brown at 216° .

The constitution of this dibromobenzenesulphonic acid (and of the diamido- and dinitro-acids from which it is derived) is determined by the following considerations. The dinitro-acid (p. 225), being formed by further nitration of metanitrobenzenesulphonic acid, has one of its NO^2 groups in the meta-position with regard to the SO^3H ; consequently the dibromo-acid formed from it by exchange of the group NO^2 for NH^2 , and of this for Br, must have one of its bromine-atoms in the meta-position with regard to the SO^3H . Now the only dibromobenzenesulphonic acids which have one of their Br-atoms thus situated are 1 : 3 : 6, 1 : 3 : 5, 1 : 3 : 4, and 1 : 2 : 3 (see diagrams, p. 227). But the first three of these are known, and differ decidedly in their properties from that last described; the latter must therefore be represented by the consecutive formula 1 : 2 : 3, and the corresponding dinitro- and diamido-acids by similar formulæ.

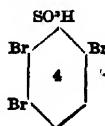
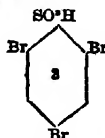
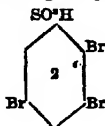
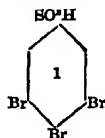
The following table exhibits a comparative view of the melting points of the chlorides and amides derived from these four dibromobenzenesulphonic acids :—

			Melting point of	
SO^3H	Br	Br	Chloride,	Amide
1	3	6	71°	193°
1	3	5	57°	203°
1	3	4	34°	175°
1	2	3	127°	216°

(5.) A fifth modification, in which the positions of the bromine-atoms have not

been determined, is obtained by treating dibromometamidobenzenesulphonic acid (p. 232) with nitrous acid, and heating the resulting diazo-compound with alcohol. The acid itself is syrupy. Its barium salt crystallises with 2 and $2\frac{1}{2}$ mols. H_2O ; the calcium salt with the same amounts of water. The chloride, $C^6H^3Br^2SO^2Cl$, forms large transparent prisms, melting at 84° ; the amide, $C^6H^3Br^2SO^2NH^2$, crystallises in white slender needles melting at 188° – 189° (Limpricht, *Deut. Chem. Ges. Ber.* viii. 1070).

ulphonic Acids, $C^6H^2Br^3SO^2H$. Of the six possible modifications of these acids five have been obtained, and the structure of four of these has been determined, three being unsymmetrical and one consecutive.



(1.) The modification 1 : 3 : 4 : 5 is obtained by substitution of Br for NH^2 in dibromoparamidobenzenesulphonic acid, $C^6SO^2H.H.Br.NH^2.Br.H$ (p. 232), which is effected by the action of hydrobromic acid on the corresponding diazo-compound. It is an easily soluble crystalline mass, forming for the most part sparingly soluble salts. The following have been examined:—

$C^6H^2Br^3SO^2(NH^2)$. Glistening microscopic plates.

$C^6H^2Br^3SO^2K$. Shining colourless plates.

$(C^6H^2Br^3SO^2)Ba + 3H^2O$. White precipitate, crystallising from hot water in thin red needles.

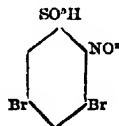
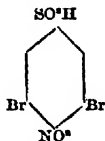
$(C^6H^2Br^3SO^2)Ca + 2\frac{1}{2}H^2O$. Slightly soluble, crystallises from hot water in six-sided microscopic needles or in long needles.

$(C^6H^2Br^3SO^2)Pb + 3\frac{1}{2}H^2O$. Precipitate, crystallising from hot water in prisms.

The chloride, $C^6H^2Br^3SO^2Cl$, crystallises in four-sided prisms, begins to soften at 123° , and liquefies at 127° .

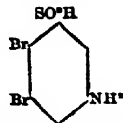
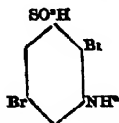
The amide, $C^6H^2Br^3SO^2NH^2$, separates from hot water as a white crystalline powder, melting at 210° (Lenz, *Deut. Chem. Ges. Ber.* viii. 1067; *Liebig's Annalen*, clxxxi. 29).

(2.) The modification 1 : 2 : 3 : 5 is produced by treating symmetrical dibromobenzenesulphonic acid with nitric acid, replacing the NO^2 -group thus introduced by NH^2 , and then the latter by Br through the diazo-reaction. Now the nitration of symmetrical dibromobenzenesulphonic acid might give rise to either of the two nitro-acids:



The first, however, treated in the manner just described, would yield the 1 : 3 : 4 : 5 modification of tribromobenzenesulphonic acid just described; but the tribrominated acid actually obtained is different from this, and yields a chloride melting at 86° , and an amide which decomposes, with blackening, when heated above 226° . The nitrodibrominated acid in question must therefore have the constitution $C^6SO^2H.NO^2.Br.H.Br.H$, and the tribromobenzenesulphonic acid formed from it must be represented by the formula, $C^6SO^2H.Br.Br.H.Br.H$ (Lenz, *Liebig's Annalen*, clxxxi. 30).

The same modification appears to be formed by passing nitrous acid vapour into concentrated hydrobromic acid holding in suspension the amidodibromobenzenesulphonic acid,



produced by the action of tin and hydrochloric acid, with aid of heat, on nitrotribromobenzenesulphonic acid (p. 247), the exchange of NH^2 for Br in either of these dibrominated acids evidently yielding the same tribrominated acid.

The tribromobenzenesulphonic acid thus produced crystallises in concentric groups of long needles easily soluble in water. Its *potassium salt*, $C^6H^3Br^3SO^3K + 2H^2O$, forms dazzling white concentrically grouped needles, easily soluble in water. The *barium salt*, $(C^6H^3Br^3SO^3)^2Ba + 6H^2O$, precipitated from the solution of the acid by barium chloride, and purified by crystallisation, forms stellate groups of white needles. The *calcium salt*, $(C^6H^3Br^3SO^3)^2Ca + 5H^2O$, forms tufts of shining needles, easily soluble in water. The *lead salt*, $(C^6H^3Br^3SO^3)^2Pb + 4H^2O$, forms white silky needles, easily soluble in water.

The chloride, $C^6H^3Br^3SO^3Cl$, forms thick rhombic plates, melting at 85.5° . The amide, $C^6H^3Br^3SO^3NH^2$, is a crystalline powder, which blackens at 220° – 230° , and decomposes at a higher temperature (Knuth, *Liebig's Annalen*, clxxxvi. 303).

(3). The modification 1 : 2 : 4 : 6 is prepared by heating symmetrical tribromobenzene with fuming sulphuric acid in sealed tubes laid upon a steam-bath. If a higher temperature is applied, large quantities of sulphurous acid are evolved; and even at the heat of the steam-bath the formation of that compound cannot be quite prevented, so that the tubes must be well cooled before they are opened. The product, a thick black mass, is poured into water; the solution filtered from unaltered tribromobenzene and insoluble products of the reaction; the filtrate neutralised with lime; and the resulting calcium salt converted into the barium salt, from which the free acid may be prepared.

The free acid crystallises in slender, easily soluble needles.

The following salts have been examined:—

$C^6H^3Br^3SO^3K + H^2O$. White, silvery, microscopic, rhombic tablets, moderately soluble in hot water.

$C^6H^3Br^3SO^3(NH^4) + H^2O$. White rhombic tablets, easily soluble in cold, still more easily in hot water.

$C^6H^3Br^3SO^3Ag + H^2O$. Concentric groups of needles, having a faint yellowish colour.

$(C^6H^3Br^3SO^3)^2Ba + 9H^2O$. Colourless or faintly reddish shining laminae, appearing under the microscope as a conglomerate of nearly square, sharply defined tablets. Slightly soluble in cold, much more freely in hot water.

$(C^6H^3Br^3SO^3)^2Ca + 7H^2O$. White silky laminae, in which, under the microscope, rhombic scales may be recognised; moderately soluble in water.

$(C^6H^3Br^3SO^3)^2Pb + 9H^2O$. White microscopic rhombic laminae having a satiny lustre; slightly soluble in cold, more easily in hot water.

The chloride, $C^6H^3Br^3SO^3Cl$, forms colourless, transparent, thick rhombic tablets, very easily soluble in ether, melting at 63° .

The amide, $C^6H^3Br^3SO^3NH^2$, separates from aqueous solution as a yellowish-red powder, in which under the microscope slender needles may be recognised. It is very slightly soluble in hot water, blackens without melting at 210° – 220° , and carbonises at a higher temperature, giving off a white sublimate (Reinke, *Liebig's Annalen*, clxxxvi. 271).

(4). The consecutive modification. 1 : 2 : 5 : 6 (SO^3H in 1), or 1 : 2 : 3 : 4 (Br in 1), is formed by exchange of NH^2 for H in the tribromometamidobenzenesulphonic acid, $C^6SO^3H.Br.NH^2.H.Br.Br$, described by Berendsen and Beckurts (p. 234). To effect the transformation, the tribromamido-acid is first converted into the corresponding diazo-compound by the action of nitrous acid on its alcoholic solution, and this compound, boiled for several hours with absolute alcohol under a pressure of 400 mm. of mercury, yields the tribromobenzenesulphonic acid, which may be obtained in the free state by evaporating the clear solution on the water-bath, dissolving the residue in water, precipitating the filtrate with barium chloride, purifying this salt by repeated crystallisation from hot water, with addition of animal charcoal, and decomposing the barium salt with dilute sulphuric acid.

The tribromobenzenesulphonic acid thus prepared crystallises from a considerable quantity of a concentrated solution, after long standing, in long transparent and colourless needles, $C^6H^3Br^3SO^3H + H^2O$, which deliquesce quickly on exposure to the air, and dissolve readily in alcohol. By decomposing the corresponding chloride, $C^6H^3Br^3SO^3Cl$, with water at 120° – 140° , an acid is obtained, crystallising in step-like groups of limpid rhombic tablets, and yielding a barium salt, differing in its quantity of crystallisation-water from that of the original acid. The acid last-mentioned softens below 100° , melts completely at that temperature, and when more strongly heated yields a sublimate of symmetric tribromobenzene (m. p. 118.5°), leaving a black tarry residue, whence it might appear to be identical with that described by Reinke, viz. 1 : 3 : 5, SO^3H (*supra*), but the salts and other derivatives of the two acids differ considerably from one another, and moreover a sulphonic acid with its

three bromine-atoms in the relative positions 1, 3, 5, could not very easily be formed from the tribromometamidobenzenesulphonic acid above mentioned: hence it is more probable that the formation of the symmetric tribromobenzene by the decomposition of the tribromobenzenesulphonic acid under consideration is due to atomic transposition.

The following salts of this acid have been investigated:—

$C^6H^3Br^3SO^3K + 3H^2O$. Shining yellow fern-like groups of laminae, crumbling into rhombic tablets when pressed.

$C^6H^3Br^3SO^3(NH^4) + H^2O$. Easily soluble white rhombic tablets having a silky lustre. $(C^6H^3Br^3SO^3)^2Ba + 8H^2O$. This salt, obtained in the original preparation of the acid, crystallises in large shining laminae, perfectly white after treatment with animal charcoal, and soluble in about 200 parts of water at 24° . The tabular acid obtained by decomposition of the chloride with hot water, yields a barium salt which crystallises in white rhombic tablets containing $(C^6H^3Br^3SO^3)^2Ba + 2H^2O$.

$(C^6H^3Br^3SO^3)^2Ca + 8H^2O$ forms light yellow needles having a silky lustre, soluble in about 45 parts of water at 23° .

$(C^6H^3Br^3SO^3)^2Pb + 6H^2O$. Shining yellowish-white rhombic laminae, soluble in about 67 parts of water at 22.5° .

$C^6H^3Br^3SO^3Ag + H^2O$. Tufts of long white needles, easily soluble and quickly blackening when exposed to light.

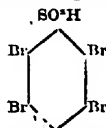
The chloride, $C^6H^3Br^3SO^3Cl$, easily prepared by the action of PCl^3 on the potassium salt, crystallises from ether in colourless rhombic prisms melting at 64.5° .

The amide, $C^6H^3Br^3SO^3NH^2$, crystallises from alcohol in white needles having a faint silky lustre, sparingly soluble in hot water, freely in alcohol. It turns brown at 220° , and volatilises with decomposition at 228° .

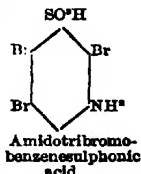
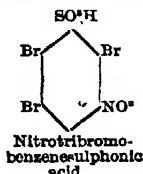
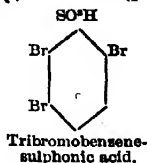
The tribromobenzenesulphonic acid just described yields, when boiled with strong nitric acid, a nitrotribromobenzenesulphonic acid, $C^6HBr^3(NO^2)SO^3H$, which, when treated with tin and hydrochloric acid, aided by continued heating, is converted into the corresponding amidotribromobenzenesulphonic acid, $C^6HBr^3(NH^2)(SO^3H)$, but when acted upon by the same reducing agent at ordinary temperatures, yields an amidodibromobenzenesulphonic acid, $C^6H^2Br^2(NH^2)(SO^3H)$.

Further, by converting the tribromamido-acid into a diazo-compound, and treating the latter with strong hydrobromic acid; a tetrabromobenzenesulphonic acid, $C^6HBr^4SO^3H$, is obtained, which crystallises from water in stellate groups of needles very soluble in water; and the dibromamido-acid, treated in like manner, yields a tribromobenzenesulphonic acid different from that just described.

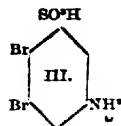
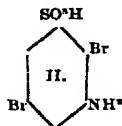
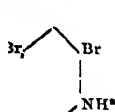
The tetrabrominated acid is identical with that described by Beckurts (p. 244), which, as shown by that chemist, has most probably the structure:—



Consequently the tribrominated acids above described, which are derivatives of *m*-amidobenzenesulphonic acid (p. 234), must be constituted as follows:—



Lastly, the amidodibrominated acid derived from the nitrotribrominated acid, by substitution of H for 1 at. Br and exchange of NO^2 for NH^2 , might have either of the following formulae:



accordingly as one or other of the bromine-atoms in the tribrominated acid is replaced by H.

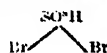
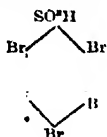
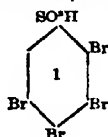
Of these, I. would yield the tribromobenzenesulphonic acid, $C^6H_3Br_3SO^3H$, identical with the one *Br* described; while II. and III. should yield the acid (1 : 2 : 3 : 5) or $C^6H_3Br_3SO^3H$, identical with that described by Lenz (p. 240). The tribrominated acid thus obtained does, in fact, agree with Lenz's acid in the character of its chloride and amide, but differs from it in the amount of crystallisation-water contained in its potassium and barium salts. For this reason, the structural formula (1 : 2 : 3 : 5) assigned to this acid must at present be regarded as not completely established (Knuth, *Liebig's Annalen*, clxxxvi. 290).

(5). A fifth tribromobenzenesulphonic acid, of unknown structure, is formed by heating the diazo-compound of amidoparadibromobenzenesulphonic acid (p. 233) with strong hydrobromic acid. The resulting liquid, evaporated down and neutralised with barium carbonate, yields a *barium salt* which, when purified by repeated crystallisation, crystallises in yellow prisms, $(C^6H_2Br_3SO^3)^2Ba + 2H^2O$. It dissolves very slowly in water, but does not crystallise out again till the solution has been very highly concentrated. The *potassium salt*, $C^6H_2Br_3SO^3K + 1\frac{1}{2}H^2O$, forms yellow shining prisms, sparingly soluble in cold, easily in hot water.

The chloride, $C^6H_2Br_3SO^3Cl$, obtained by heating the potassium salt to 130° in a sealed tube with PCl_5 and $POCl_3$, remained in the solid form on washing the product with water, but separated from ether as an oil.

The amide, $C^6H_2Br_3SO^3NH_2$, obtained by heating the chloride to 110° in a sealed tube with concentrated ammonia, forms small needles, which dissolve without much difficulty in alcohol, begin to turn brown at 200° , and melt, with rapid decomposition, when heated above 220° (Borns, *Liebig's Annalen*, clxxxvi. 364).

Tetrabromobenzenesulphonic Acid, $C^6HBr_4SO^3H$. Of this acid there are three modifications, one derived from each of the three tetrabromobenzenes, viz. :—



(1). The modification 1 : 2 : 3 : 4 : 5 is formed from tribromobenzenesulphonic acid, $C^6H_3Br_3SO^3H$, by converting this acid into the nitro-brominated acid, $C^6H_2Br_3NO^3$, this latter into the corresponding amido-acid, and replacing the NH_2 -group therein by Br through the medium of the diazo-compound.

This tetrabrominated acid is a crystalline precipitate which separates from hot water in microscopic plates. The *barium salt*, $(C^6HBr_4SO^3)^2Ba + H^2O$, is sparingly soluble in cold water and crystallises from a hot solution in transparent rhombic needles. The chloride, $C^6HBr_4SO^3Cl$, crystallises in small rhombic needles melting at 120° . The amide is a crystalline powder melting at 181° (Lenz, *Liebig's Annalen*, clxxxi. 23).

(2). The modification 1 : 2 : 3 : 4 : 6, in which the four bromine-atoms are arranged unsymmetrically, is formed from (1 : 2 : 4 : 6) tribromobenzenesulphonic acid (p. 241) by a series of processes exactly similar to those by which the preceding modification is obtained from the tribrominated acid (1 : 3 : 4 : 5). It is very soluble in water, less soluble in alcohol, and crystallises from aqueous solution in needles and six-sided plates, which melt when heated on platinum foil. The following salts have been prepared :—

$C^6HBr_4SO^3K$ (anhydrous). Silky microscopic needles or prisms easily soluble in water.

$C^6HBr_4SO^3(NH_4)$ (anhydrous). Prepared from the calcium salt by the action of ammonium carbonate. Faintly reddish shining rhombic plates, easily soluble in water.

$(C^6HBr_4SO^3)^2Ba + 1\frac{1}{2}H^2O$. Microscopic rhombic prisms, slightly soluble in cold and hot water.

$(C^6HBr_4SO^3)^2Ca + 8H^2O$. Delicate faintly reddish needles, appearing under the microscope as rhombic prisms; very soluble in water.

$(C^6HBr_4SO^3)^2Pb + 1\frac{1}{2}$ and $2H^2O$. Obtained by saturating the acid with lead carbonate; separates from a hot saturated solution as a brownish crystalline powder made up of microscopic six-sided prisms containing $2H^2O$. By slow evaporation, somewhat larger rhombic prisms are formed containing $1\frac{1}{2}H^2O$.

The chloride, $C^6HBr_4SO^3Cl$, crystallises in stellate groups of colourless or faintly brownish laminae, easily soluble in ether, caking together at 85° , and melting completely at 91° .

The amide, $C^6HBr_4SO^3NH_2$, separates from water as a white powder, and from alcohol in tufts of microscopic needles, slightly soluble in water, easily in alcohol.

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blackens at 250° without previous fusion, but melts on platinum foil and burns away, with previous emission of white fumes (Reinke, *Liebig's Annalen*, clxxxvi. 232).

(3). The modification 1 : 2 : 3 : 5 : 6, with symmetrically disposed bromine-atoms, is obtained from (1 : 2 : 5 : 6) tribromobenzenesulphonic acid, in the same manner as the two preceding modifications from the corresponding tribrominated acids. It is easily soluble in water and in alcohol, and crystallises in stellate groups of needles which carbonise without melting when heated.

The *potassium salt*, $C^6HBr^4SO^3K$ (anhydrous), forms small white needles easily soluble in water. The *ammonium salt*, $C^6HBr^4SO^3(NH^4)$, forms reddish laminae. The *barium salt*, $(C^6HBr^4SO^3)^2Ba + 1\frac{1}{2}H^2O$, forms delicate white laminae (Beckurts). According to Knuth, the solution of the acid gives with barium chloride a precipitate which dissolves in hot water, and separates from the solution in finely reddish needles. The *calcium salt*, $(C^6HBr^4SO^3)^2Ca + 8H^2O$, crystallises in ~~the~~ white needles; the *lead salt*, $(C^6HBr^4SO^3)^2Pb + 4H^2O$, in small prisms; the *silver salt*, $C^6HBr^4SO^3Ag + 1\frac{1}{2}H^2O$ (?) in small hexagonal prisms. These salts are sparingly soluble in cold water (Beckurts).

The chloride, $C^6HBr^4SO^2Cl$, crystallises in reddish rhombic plates easily soluble in ether, melting at 91·5° (Beckurts), at 93° (Knuth).

The amide, $C^6HBr^4SO^2NH^2$, crystallises from alcohol in white microscopic needles, slightly soluble in hot water, easily in alcohol, becoming discoloured at 300° and melting at a higher temperature (Beckurts, *Liebig's Annalen*, clxxxi. 217; Knuth, *ibid.* clxxxvi. 282).

Pentabromobenzenesulphonic Acid, $C^5Br^5SO^3H$, formed by the action of hot hydrobromic acid on the diazo-compound of amidotetrabromobenzenesulphonic acid, $C^5Br^4(NH^2)SO^3H$ (either modification), crystallises in slender laminae and needles, which dissolve very sparingly in water. When heated to 180°–200° it evolves sulphur dioxide, and yields a sublimate of white needles (probably pentabromobenzene), leaving charcoal. It is not affected by boiling with the strongest nitric acid or potash.

The *ammonium salt*, $C^5Br^5SO^3NH^4$, crystallises from hot water in white laminae. The *potassium salt*, $C^5Br^5SO^3KH^2O$, forms microscopic quadrate prisms. The *barium salt*, $(C^5Br^5SO^3)^2Ba + 1\frac{1}{2}H^2O$, forms delicate laminae. The *calcium salt*, $(C^5Br^5SO^3)^2Ca + 4H^2O$, forms white prisms. The *silver salt*, $C^5Br^5SO^3Ag + 1\frac{1}{2}H^2O$, is a white crystalline powder. All the salts dissolve sparingly in cold water.

The chloride, $C^5Br^5SO^2Cl$, crystallises in needles which melt at 90°. The amide, $C^5Br^5SO^2NH^2$, is deposited from hot water as a crystalline powder, soluble in alcohol. It blackens without melting at 256°.

Nitrobromobenzenesulphonic Acids, $C^6H^3BrNO^2SO^3H$ (Goslich, *Liebig's Annalen*, clxxx. 93; Limpricht, *Deut. Chem. Ges. Ber.* viii. 456). Para- and meta-bromobenzenesulphonic acid are converted into the corresponding mononitro-acids by treating their barium salts with the strongest nitric acid, decanting the liquid from the barium nitrate which separates out, and expelling the excess of nitric acid by evaporation over the water-bath. The residue may then be converted into barium salt, and the other salts prepared therefrom.

The following table exhibits a comparative view of the salts of these two acids :—

	<i>Para.</i>	<i>Meta.</i>
$C^6H^3Br(NO^2)SO^3NH^4$	Yellow laminae, decomposing at 180°	Long yellow prisms
$C^6H^3Br(NO^2)SO^3K$	Sparingly soluble yellow laminae	
$[C^6H^3Br(NO^2)SO^3]^2Ba$	+ $1\frac{1}{2}H^2O$. Sparingly soluble yellow laminae	+ $3H^2O$. Small yellow prisms
$[C^6H^3Br(NO^2)SO^3]^2Ca$	+ $2\frac{1}{2}H^2O$. Nearly white slender needles	
$[C^6H^3Br(NO^2)SO^3]^2Pb$	+ $2H^2O$. Nodular groups of yellow needles	+ $3H^2O$. Yellow nodules

Nitro-*para* bromobenzenesulphonic chloride, $C^6H^3Br(NO^2)SO^2Cl$, crystallises from a mixture of ether and benzoin in yellow prisms melting at 56°–57°. The corresponding *amide*, $C^6H^3Br(NO^2)SO^2NH^2$, crystallises in light yellow micaceous laminae, melting at 177° (Goslich).

Ammonium nitrometabromobenzenesulphonate, heated to 180° with alcoholic ammonia, is converted into the corresponding *nitrometamidobenzenesulphonate*, and by treatment with ammonium sulphide into the *amidometabromobenzenesulphonate* (Limpricht).

BENZENESULPHONIC ACIDS (NITRODIBROMO-). 245

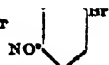
The positions of the nitro-group in the two acids just described have not been determined. Parabromobenzenesulphonic acid can give rise to two, and metabromobenzenesulphonic acid to four mononitro-derivatives.

Nitro-orthobromobenzenesulphonic acids.—Two of these acids are formed by direct nitration of orthobromobenzenesulphonic acid. The dry bromo-acid is heated in a porcelain basin with the strongest nitric acid, and as soon as the violent reaction is over, the liquid is evaporated to dryness on the water-bath. There then remains a yellow crystalline residue consisting of two nitrobrominated acids, which may be separated by neutralising the mixture with barium carbonate, and recrystallising the resulting barium salts several times; at first yellow needles separate out, causing the whole to solidify if the solution is somewhat concentrated; and afterwards small prisms, consisting of a mixture of the two isomeric acids, which may be further separated by evaporating the entire mother-liquor to dryness, drenching the remaining residue with warm water at 60°–60°, and filtering quickly. The undissolved barium salt, recrystallised with addition of animal charcoal, separates in white nacreous laminae.

The nitro-acid whose barium salt crystallises in needles is formed in much larger

SO³H

quantity than the other, and has the structure 1 : 2 : 5, or



The yellow

needles of its barium salt, which separate in the first instance, may be rendered perfectly white by recrystallisation with the aid of animal charcoal. The free acid, obtained by decomposing this salt with dilute sulphuric acid, and evaporating the filtrate, crystallises in large, flat, slightly yellowish prisms containing 2 mols. H₂O, very easily soluble in water and alcohol. The crystals heated to 110° give off their water very slowly without fusion, but at 130°–135°, they melt and give it off very quickly.

The following salts of this acid have been examined:—

C⁶H³Br(NO²).SO³.NH⁴. Slender white anhydrous needles, easily soluble in water.

The potassium and sodium salts are likewise anhydrous, and resemble the ammonium salt in form and solubility.

C⁶H³Br(NO²).SO³.Ag. Yellow needles, somewhat sparingly soluble in water, and becoming darker in colour on exposure to light.

[C⁶H³Br(NO²).SO³]².Ba + 5H₂O. Long, ramified, white, silky needles, easily soluble in hot, sparingly in cold water.

[C⁶H³Br(NO²).SO³]².Ca + 4H₂O. White shining needles very soluble in water.

[C⁶H³Br(NO²).SO³]².Zn + 7H₂O. Well-defined, thick, transparent, colourless prisms, easily soluble in water.

[C⁶H³Br(NO²).SO³]².Pb + 5H₂O. White slender needles, easily soluble in water.

The chloride, **C⁶H³Br(NO²).SO³.Cl.** forms large thick rhombic tablets melting at 42°. The amide, **C⁶H³Br(NO²).SO³.NH²,** forms white shining needles, moderately soluble in hot, sparingly in cold water, melting at 205°.

This nitrobromobenzenesulphonic acid, reduced with tin and hydrochloric acid, yields an amidobrominated acid, the diazo-compound of which is converted by heating with hydrobromic acid into paradibromobenzenesulphonic acid, **C⁶.SO³H.Br.H.H.Br.H.** The reaction shows that the NH² in the amido-acid, and consequently the NO²-group in the nitro-acid, is in the para-position with respect to the Br; hence the formula above given.

Nitrodibromobenzenesulphonic Acids. 1. **Nitroparadibromobenzenesulphonic acid,** **C⁶H²Br(NO²).SO³H + 1½H₂O** (Borns, *Liebigs Annalen*, cxxxvii. 358).—This acid is obtained by boiling paradibromobenzenesulphonic acid in a retort with the strongest nitric acid for about an hour. If the heating be stopped after a shorter time, or if the operation be conducted in a porcelain dish, part of the dibromo-acid remains unaltered, and if the heating be longer continued, dinitrodibromobenzenesulphonic acid is likewise produced. As soon as the greater part of the nitric acid has been distilled off, the remaining liquid is evaporated in a basin on the water-bath, the yellow crystalline residue is dissolved in water, the solution neutralised with barium carbonate, and the resulting barium salt crystallised. This process appears to yield only one nitroparadibromobenzenesulphonic acid, although three modifications are possible. The position of the nitro-group in this acid is not yet determined.

The acid, separated by sulphuric acid from its barium salt, crystallises, on evaporation over sulphuric acid, in small light yellow very hygroscopic prisms which dissolve easily in alcohol and in ether, and blacken at 100° without melting.

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The *ammonium salt*, $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{SO}_2\text{NH}_4 + 0.5\text{H}_2\text{O}$, forms small laminae and nodules, which dissolve easily in water, alcohol, and ether, give off their water of crystallisation at 131° , and decompose on prolonged heating to 150° . Heated with alcoholic ammonia it gives off part of its bromine.

The *potassium salt*, $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{SO}_2\text{K} + \text{H}_2\text{O}$ ($2\frac{1}{2}\text{H}_2\text{O}$), according to Hübner a. Williams, crystallises in groups of yellow needles easily soluble in water and in alcohol.

The *barium salt*, $[\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\text{SO}_2]_2\text{Ba}$, like the corresponding paradibromobenzenesulphonate, exhibits a marked tendency to unite with different quantities of water. With 1.5 mol. H_2O , which is the most usual amount, it crystallises in yellow shining prisms, easily soluble in hot, sparingly in cold water. With $6\text{H}_2\text{O}$ it forms shining yellow needles, like those of the potassium salt, or nodular groups of prisms; with $9\text{H}_2\text{O}$, small yellow nodules. Williams obtained a barium salt with $2.5\text{H}_2\text{O}$; Limprieth obtained one with 1 mol. H_2O .

The *calcium salt*, $[\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\text{SO}_2]_2\text{Ca} + 3\text{H}_2\text{O}$, forms light yellow prisms easily soluble in water and in alcohol.

The *lead salt*, $[\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\text{SO}_2]_2\text{Pb} + 3\text{H}_2\text{O}$, forms yellow nodules easily soluble in water and in alcohol. Hübner a. Williams obtained a lead salt with $2\text{H}_2\text{O}$, which they described as sparingly soluble.

The *chloride*, $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{SO}_2\text{Cl}$, obtained by heating the potassium salt with PCl_5 and POCl_3 in a sealed tube to 120° , forms, after washing with water, a white mass, easily soluble in alcohol and ether, sparingly in light petroleum, and separates from the ethereal solution as a thick oil containing a few crystals which, however, could not be separated from the oil sufficiently well to admit of a determination of the melting point.

The *amide*, $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{SO}_2\text{NH}_2$, is also difficult to prepare, but is best obtained by heating the chloride with strong ammonia to 100° in a sealed tube; after repeated crystallisation from hot water and alcohol, it forms small greenish-yellow needles sparingly soluble in cold, easily in hot water and in alcohol, melting at 178° .

2. *Nitrometadibromobenzenesulphonic acid*.—The acid produced by nitration of symmetrical dibromobenzenesulphonic acid has, as already observed (p. 240), the constitution $\text{C}_6\text{H}_2\text{Br}_2\text{NO}_2\cdot\text{Br}\cdot\text{H}\cdot\text{Br}\cdot\text{H}$. To prepare it, dried and pulverised barium dibromobenzenesulphonate is added to nitric acid of sp. gr. 1.5 by small portions, so as not to produce perceptible rise of temperature; the liquid, after standing for twenty-four hours, is decanted from the precipitated barium nitrate; this precipitate is drained on an asbestos filter; and the liquid is evaporated on the water-bath till the excess of nitric acid is completely driven off. The syrupy residue left over sulphuric acid deposits a few crystals of the nitrodibrominated acid in the form of colourless elongated tablets, which however cannot be completely separated from the mother-liquor. They effloresce over sulphuric acid, and therefore contain water of crystallisation; they are not hygroscopic, but dissolve very easily in water, easily also in alcohol (of 95 p.c.), and in ether. The dilute solution gives a precipitate with lead acetate; the more concentrated solution with barium chloride and potassium carbonate.

The following salts of this acid have been examined:—

$\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{SO}_2(\text{NH}_4) + \text{H}_2\text{O}$. Obtained by neutralisation. Forms small solid colourless crystals, easily soluble in water, sparingly in alcohol of 95 p.c. By heating the dried salt to 230° with alcoholic ammonia, it appears to be converted into the ammonium salt of *bromonitramidobenzenesulphonic acid*, $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)(\text{NH}_2)\cdot\text{SO}_2\text{H}$.

$\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{SO}_2\text{K} + \text{H}_2\text{O}$, obtained by neutralisation, forms delicate, shining, colourless, brittle laminae, appearing under the microscope to consist of right-angled parallelograms; moderately soluble in water.

$[\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\text{SO}_2]_2\text{Ba} + 1\frac{1}{2}$ and $4\text{H}_2\text{O}$. When the concentrated solution of the acid is precipitated by barium chloride, and the precipitate dissolved in hot water, the solution on cooling first deposits yellowish obtuse rhombohedrons containing $1\frac{1}{2}\text{H}_2\text{O}$, afterwards thin rhombic plates containing $4\text{H}_2\text{O}$: the two forms are, however, so much intergrown that complete separation is impossible. Both are but sparingly soluble in water.

$[\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\text{SO}_2]_2\text{Ca} + 3\text{H}_2\text{O}$, obtained by neutralising the acid with chalk and leaving the concentrated solution to evaporate at ordinary temperatures, is a colourless powder, appearing under the microscope as a collection of small laminae often grouped in geodes; easily soluble in water.

$[\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\text{SO}_2]_2\text{Pb} + 5\text{H}_2\text{O}$ is precipitated by lead acetate from the dilute solution of the acid, and separates from solution in hot water as a colourless powder, appearing under the microscope to consist of geodes of ill-defined laminae; sparingly soluble in hot, very sparingly in cold water.

The *chloride*, $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{SO}_2\text{Cl}$, forms transparent colourless nearly rect-

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angular plates, rather sparingly soluble in ether, softening at 118° and melting at 121° . The amide, $C^6H^2Br^3(NO^2).SO^2NH^2$, is formed, with violent reaction, by heating the chloride with strong ammonia, and separates from hot water in geodes of indistinct microscopic crystals, slightly soluble in cold water, easily in hot water and in alcohol.

By converting this nitrodibrominated acid into the corresponding amido-acid, the latter into the diazo-compound, and heating this last compound with concentrated hydrobromic acid, a tribromobenzenesulphonic acid is obtained, having the unsymmetric structure 1 : 2 : 3 : 5, or $SO^2H.Br.Br.H.Br.H$ (Lens, *Liebig's Annalen*, clxxxi. 33-39).

3. *Nitro-orthodibromobenzenesulphonic acid*, $C^6H^2Br^2(NO^2).SO^2H.H.Br.Br.H^2$. The latter is dehydrated, first over the water-bath, afterwards over an open flame; the crystalline cake which remains is heated in a capacious retort with the strongest nitric acid till the excess of nitric acid passes over colourless; and the remaining nitric acid is expelled by evaporation in a basin. The highly concentrated solution solidifies to a yellow crystalline mass, hygroscopic and extremely soluble in water.

The following salts have been prepared:—

$C^6H^2Br^2(NO^2).SO^2NH^2$ (anhydrous). Moderately soluble needles having a deep yellow colour.

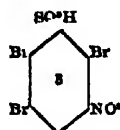
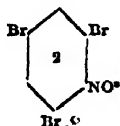
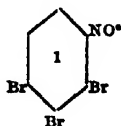
$[C^6H^2Br^2(NO^2).SO^2]^2Ba + 3H^2O$. Faintly yellow needles grouped in small nodules; easily soluble in hot, sparingly in cold water.

$[C^6H^2Br^2(NO^2).SO^2]^2Ca + 4H^2O$ and $6H^2O$. Very much like the barium salt, but much more soluble in water. Crystallises for the most part in nodular groups of slender microscopic needles with $4H^2O$; sometimes also in stellate groups of long transparent needles containing $6H^2O$.

$[C^6H^2Br^2(NO^2).SO^2]^2Pb + 3H^2O$. Slender needle-shaped light yellow needles.

The chloride, $C^6H^2Br^2(NO^2).SO^2Cl$, formed by heating the potassium salt with PCl^5 and $POCl^3$ to 140° in a sealed tube, crystallises from ether in small needles, melting at 98° - 99° . The amide, $C^6H^2Br^2(NO^2).SO^2NH^2$, forms felted groups of white slender needles, very slightly soluble in cold water, easily in hot water and hot alcohol, melting at 210° - 211° .

Nitrotribromobenzenesulphonic Acids, $C^6HBr^3(NO^2).SO^2H$. Out of ten* possible modifications of these acids, the three following are known:—



1. The first modification, produced by nitration of 1 : 3 : 4 : 5 tribromobenzenesulphonic acid, crystallises from its concentrated syrupy solution in colourless laminae, very soluble in water, easily in alcohol and ether; strong hydrochloric acid precipitates it from the aqueous solution as a crystalline pulp.

$C^6H(NO^2)Br^3.SO^2(NH^2) + H^2O$ crystallises in small, flat, dazzling white needles, easily soluble in water, less soluble in alcohol.

$C^6HBr^3(NO^2).SO^2K + H^2O$ separates almost completely on neutralising the aqueous solution with potassium carbonate, and crystallises from a hot aqueous solution on cooling, in sandy grains made up of microscopic laminae.

$[C^6HBr^3(NO^2).SO^2]^2Ba + 4H^2O$ is obtained by precipitation, and crystallises from hot water in splendid colourless prisms having a silky lustre.

$[C^6HBr^3(NO^2).SO^2]^2Ca + 3H^2O$, obtained by neutralisation, forms colourless microscopic laminae grouped in geodes.

$[C^6HBr^3(NO^2).SO^2]^2Pb + H^2O$, precipitated from a solution of the acid by lead acetate, and recrystallised, forms a white powder composed of groups of microscopic

The chloride, $C^6HBr^3(NO^2).SO^2Cl$, forms microscopic crystalline geodes melting at 116° ; the amide, $C^6HBr^3(NO^2).SO^2NH^2$, is a crystalline powder, melting at 202° .

This nitrotribrominated acid, treated with tin and hydrochloric acid, is converted into the corresponding amidotribrominated acid, which crystallises in easily soluble slender needles, and forms a precipitate with barium chloride.

The corresponding diazo-compound crystallises from alcohol in colourless needles and when decomposed by hydrobromic acid, yields tetrabromobenzenesulphonic acid

248 BENZENESULPHONIC ACIDS (NITROTETRABROMO-)

$C^6SO^4H.Br.Br.Br.Br.H$ (p. 243), (Limpricht & Lenz, *Deut. Chem. Ges. Ber.* viii. 1072, 1492; Lenz, *Liebigs Annalen*, clxxxi. 41).

2. The second modification, $C^6SO^4H.Br.NO^2.Br.H.Br.$ is prepared by boiling (1 : 2 : 4 : 6) tribromobenzenesulphonic acid (p. 243) with the strongest nitric acid in a retort for an hour, evaporating the solution to dryness over a water-bath, and drenching the residue with water. There then remains a yellowish crystalline compound, probably $C^6NO^2.Br.Br.Br.H^2$ (p. 180); and the aqueous solution when evaporated yields the nitrotribromobenzenesulphonic acid in stellate groups of microscopic needles and square prisms, easily soluble in water, somewhat less soluble in alcohol, sparingly in ether. The crystals heated in a test-tube melt somewhat above 100° , and turn brown at 160° ; on platinum foil they burn away rapidly. The aqueous solution gives precipitates with barium chloride and lead acetate.

$C^6HBr^4(NO^2).SO^4NH^4$ crystallises in concentric groups of faintly yellowish anhydrous needles, appearing under the microscope as nearly rectangular prisms. Easily soluble in water.

$C^6HBr^4(NO^2).SO^4K$. Stellate groups of easily soluble faintly yellowish needles.

$[C^6HBr^4(NO^2)SO^4]^2Ba + 1\frac{1}{2}H^2O$. Shining white crystalline powder, made up of microscopic rhombic tablets; sparingly soluble in water, hot or cold.

$[C^6HBr^4(NO^2)SO^4]^2Ca + 2H^2O$. White nearly rectangular microscopic prisms, easily soluble in water.

$[C^6HBr^4(NO^2)SO^4]^2Pb + 1\frac{1}{2}H^2O$. White shining crystalline powder, consisting of microscopic rhombic tablets, very soluble in water.

The chloride, $C^6HBr^4(NO^2).SO^4Cl$, is difficult to prepare, and was only once obtained, by treating the crude product with light petroleum, as a solid body sparingly soluble in that liquid, and turning brown at 160° without melting. The amide is a faintly yellowish crystalline powder, which dissolves sparingly in water, easily in alcohol, and turns brown at 210° without previous fusion.

This nitro-acid, treated with tin and hydrochloric acid, yields the corresponding amidotribromobenzenesulphonic acid, and the diazo-compound prepared therefrom is converted by hydrobromic acid into tetrabromobenzenesulphonic acid, $C^6SO^4H.Br.Br.Br.Br.H.Br.$ (p. 243), (Reinke, *Liebigs Annalen*, clxxvi. 278).

3. The third modification, $C^6SO^4H.Br.NO^2.H.Br.Br.$ formed similarly to the preceding, by nitration of (1 : 2 : 5 : 6) tribromobenzenesulphonic acid, remains, on evaporating its aqueous solution, in stellate groups of yellowish-white microscopic prisms, which deliquesce on exposure to the air, dissolve very easily in alcohol, less easily in ether. When heated in a glass tube, it yields a sublimate of symmetric tribromobenzene (by atomic transposition).

$C^6HBr^4(NO^2).SO^4K + 1\frac{1}{2}H^2O$. Radiate groups of white shining needles, easily soluble in hot, slightly in cold water.

$[C^6HBr^4(NO^2)SO^4]^2Ba + 10H^2O$. Precipitate slightly soluble in hot water, and separating slowly therefrom in stellate groups of yellow needles, which may be decolourised by treatment with animal charcoal.

$[C^6HBr^4(NO^2)SO^4]^2Ca + 3\frac{1}{2}H^2O$. Shining white microscopic laminae, easily soluble in water.

The chloride forms flat rhombic plates with truncated angles, turning brown at 126° , and melting at 142° . The amide crystallises in microscopic yellow needles having a faint silky lustre; dissolves easily in alcohol, sparingly in water; turns brown at 160° and melts at 175° .

The diazo-compound of the corresponding amidotribrominated acid is converted by concentrated hydrobromic acid into (1 : 2 : 3 : 5 : 6) tetrabromobenzenesulphonic acid (p. 243).

Nitrotetrabromobenzenesulphonic Acid, $C^6SO^4H.Br.Br.NO^2.Br.Br.$ This acid, formed by nitration of the tetrabromobenzenesulphonic acid with symmetrically situated bromine-atoms, is the only one of the three possible acids, $C^6Br^4(NO^2).SO^4H$, at present known. It is prepared by boiling the tetrabrominated acid with strong nitric acid in a retort for a considerable time, and remains, on evaporating the solution over a water-bath, as a yellowish-white crystalline residue. After recrystallisation from hot water, it forms yellowish-white, shining, brittle needles containing $4H^2O$, easily soluble in hot, less soluble in cold water, soluble also in alcohol. The following salts have been examined:—

$C^6Br^4(NO^2).SO^4(NH^4) + H^2O$. Separates, on cooling from a hot solution, as a white powder made up of small plates; soluble in about 92 parts of water at 11° .

$C^6Br^4(NO^2).SO^4K + 1\frac{1}{2}H^2O$. Obtained in like manner, in fine prisms having a satiny lustre, soluble in about 175 pts. of water at 10.5° .

$[\text{C}^6\text{Br}(\text{NO}^2\text{SO}^2)^2]_2\text{Ba} + 9\text{H}^2\text{O}$. Small, flat, yellowish-white, very brittle prisms, soluble in about 275 pts. water at 10.5° .

$[\text{C}^6\text{Br}(\text{NO}^2\text{SO}^2)^2]_2\text{Ca} + 8\text{H}^2\text{O}$. Crystallises on cooling in delicate white laminae, very slightly soluble in water (1 pt. in about 637 pts. at 6°).

$[\text{C}^6\text{Br}(\text{NO}^2\text{SO}^2)^2]_2\text{Pb} + 9\text{H}^2\text{O}$. Large nacreous prisms, very slightly soluble in water (1 pt. in about 1670 pts. at 5°).

$\text{C}^6\text{Br}(\text{NO}^2\text{SO}^2)\text{Ag} + \text{H}^2\text{O}$. Slender white needles, quickly turning brown in contact with the air.

The chloride, $\text{C}^6\text{Br}(\text{NO}^2\text{SO}^2)\text{Cl}$, prepared by heating the potassium salt with the calculated quantity of PCl^5 and a little $\cdot\text{POCl}^3$ to 120° – 130° (at 180° hexachlorobenzene is produced), crystallises from ether in delicate white rhombic plates, melting at 146° – 147° .

The amide, $\text{C}^6\text{Br}(\text{NO}^2\text{SO}^2)\text{NH}^2$, is a crystalline powder very slightly soluble in water, easily soluble in alcohol, and crystallising therefrom in concentric groups of microscopic needles. It remains solid at 300° , but melts to a dark liquid when heated in a test-tube over an open flame, and decomposes at a higher temperature with emission of white fumes (Beckurts, *Liebig's Annalen*, clxxxi, 220).

Chlorobenzenesulphonic Acids, $\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2\text{H}$ (Limpricht, *Deut. Chem. Ges. Ber.* viii, 1070; Goslich, *Liebig's Annalen*, clxxx, 106; Kieselinsky, *ibid.* 108). These acids are formed from the amidobenzenesulphonic acids, by processes similar to those employed for the preparation of the corresponding brominated acids.

Parachlorobenzenesulphonic acid, $\text{C}^6\text{SO}^2\text{H}\cdot\text{H}\cdot\text{H}\cdot\text{Cl}\cdot\text{H}^2$, is formed, with evolution of nitrogen, by heating the diazo-compound of paramidobenzenesulphonic acid with strong hydrochloric acid. The syrupy residue left after expulsion of the hydrochloric acid is diluted with water and neutralised with barium carbonate, and the impure barium salt thus obtained is converted into the potassium salt, which, on treatment with phosphorus pentachloride, yields the corresponding chloride; the latter is converted by ammonia into the amide, which is easily purified, and when treated with hydrochloric acid yields parachlorobenzenesulphonic acid.

The barium and lead salts of this acid form tabular crystals containing 1 mol. water.

The chloride, $\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2\text{Cl}$, crystallises in flat transparent prisms melting at 53° .

The amide, $\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2\text{NH}^2$ forms white laminae melting at 143° – 144° (Goslich).

This chlorobenzenesulphonic acid is identical with that which was obtained by Otto a. Brunner and by Glutz, by treating chlorobenzene with fuming sulphuric acid (1st Suppl. 274), whence it appears that the chlorinated acid, like the bromobenzenesulphonic acid obtained by dissolving bromobenzene in sulphuric acid, is a para-compound. It is true that the chlorobenzenesulphonic acid thus formed yields resorcin when fused with potash; but it has been shown in many instances that this reaction cannot be relied on for determining the relative positions of the substituted radicles in aromatic compounds (Limpricht).

Meta-chlorobenzenesulphonic acid, $\text{C}^6\text{SO}^2\text{H}\cdot\text{H}\cdot\text{H}\cdot\text{Cl}\cdot\text{H}^2$, is formed by the action of hydrochloric acid on the diazo-compound of metamidobenzenesulphonic acid, and purified in the same manner as the para-acid. The pure acid crystallises in pearly laminae and tables which deliquesce in the air, and dissolve readily in alcohol. Its salts are not decomposed at 200° . The potassium salt, $\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2\text{K}$, is very soluble in water, and crystallises from alcohol in white shining laminae. The barium salt, $(\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2)_2\text{Ba} + 2\text{H}^2\text{O}$, forms shining rhombic plates which effloresce in the air, and dissolve with difficulty in cold water and alcohol, more easily in the same liquids when warm.

The calcium salt, $(\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2)_2\text{Ca}$ (anhydrous), forms white rhombic plates, very easily soluble in water, less soluble in alcohol. The copper salt, $(\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2)_2\text{Cu} + 5\text{H}^2\text{O}$, separates from its aqueous solution by slow evaporation in transparent nacreous prisms very easily soluble in water, sparingly in alcohol. The silver salt, $\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2\text{Ag}$ (anhydrous), obtained by neutralising the acid with silver carbonate, forms highly lustrous rhombic tables and laminae, which become dark-coloured on exposure to light, and are very soluble in water. The chloride, $\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2\text{Cl}$, is an oily liquid which dissolves easily in ether, and does not solidify even in a freezing mixture.

The amide, $\text{C}^6\text{H}^4\text{Cl}\cdot\text{SO}^2\text{NH}^2$, forms large transparent tables, easily soluble in alcohol, ether, and hot water, sparingly in cold water; melting at 148° (Kieselinsky).

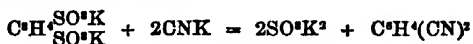
Orthochlorobenzenesulphonic acid, $C^6H^4SO^2H.Cl.H^4$, is obtained by heating the diazo-compound of orthamidobenzenesulphonic acid with hydrochloric acid saturated at 0° , in a flask under a pressure of 300 mm. of mercury. Its chloride, prepared in the usual way, and purified by solution in ether, separates therefrom as an oily liquid, which cannot be made to crystallise even in a freezing mixture; but by converting it into the amide, purifying this compound by crystallisation, and heating it to 180° in sealed tubes with hydrochloric acid, so as to re-convert it into the acid, and heating the potassium salt of this purified acid with PCl^3 and $POCl^3$, a chloride, $C^6H^4SO^2Cl.Cl.H^4$, is obtained, which easily crystallises from ether in thick colourless prisms, melting at 28.5° . The amide, prepared from this solid chloride, melts at 188° (Bahlmann, *Liebig's Annalen*, clxxxvi. 325).

Orthiodobenzenesulphonic Acid, $C^6H^4SO^2H.I.H^4$. Prepared from the diazo-compound of the *o*-amido-acid with fuming hydriodic acid, forms a *potassium salt*, $C^6H^4SO^2K.I.H^4 + H^2O$, which crystallises in well-defined, apparently monoclinic crystals, sparingly soluble in water. Its *barium salt*, $(C^6H^4ISO^2)^2Ba$, crystallises in small white anhydrous needles, sparingly soluble in cold, easily in hot water. The chloride, $C^6H^4SO^2Cl.I.H^4$, prepared from the potassium salt with PCl^3 , crystallises from ether in thick transparent colourless prisms which melt at 51° . The amide, $C^6H^4SO^2NH^2.I.H^4$, forms thin white slightly soluble laminæ melting at 170° (Bahlmann, *loc. cit.*)

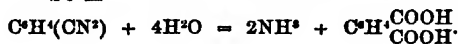
The following table exhibits the melting points of the chlorides and amides of the orthonitro-, chloro-, bromo-, and iodo-benzenesulphonic acids, as determined by

	Chloride	Amide
Orthonitrobenzenesulphonic.	67°	188°
Orthochlorobenzenesulphonic	28.5°	188°
Orthobromobenzenesulphonic	51°	186°
Orthiodobenzenesulphonic	51°	170°

Benzenedisulphonic Acids, $C^6H^4(SO^2H)^2$. The *monosulphonic acid*, $C^6H^4SO^2H$, heated with oil of vitriol, is converted into a disulphonic acid, $C^6H^4(SO^2H)^2$, the potassium salt of which, distilled with potassium cyanide, yields a dicyanobenzene or phenylene dicyanide, $C^6H^4(CN)^2$, and this, when distilled with an alkali, is converted into the corresponding dicarbon-acid;



and



Now Wislicenus a. Brunner found that the dicarbon-acid thus produced was terephthalic acid (*2nd Suppl.* 152), and the same result was obtained by Ross-Garrick (*Zeitschr. f. Chem.* v. 549), whence it would appear that the disulphonic acid obtained as above is a *para*-compound. Barth a. Senhofer, on the other hand (*Liebig's Annalen*, clxxiv. 238), obtained by the same process, not terephthalic but isophthalic acid, from which it would follow that the disulpho-acid in question is a *meta*-compound. This discrepancy has been explained by the experiments of V. Meyer a. Michler (*Deut. Chem. Ges. Ber.* viii. 672), and by the further experiments of Barth a. Senhofer (*ibid.* 754), which have shown that the dicarbon-acid obtained by the series of processes above indicated is always a mixture of isophthalic and terephthalic acids, and consequently that the disulphonic acid formed by heating benzenemonosulphonic acid with sulphuric acid is a mixture of the *meta*- and *para*-benzenedisulphonic acids, the one or the other prevailing according to the degree of heat applied and the duration of the reaction. At the commencement of the reaction, and while the temperature is comparatively low, the product consists mainly of *meta*-disulphonic acid, but if the action is prolonged and the temperature raised, the *para*-acid is chiefly produced.

Körner a. Monselise (*Gazz. chim. ital.* 1876, p. 133) prepare the two benzenedisulphonic acids by dissolving 2 pts. of pure benzene in 3 pts. of a mixture of ordinary (1 vol.) and fuming (2 vols.) sulphuric acid, and heating the product with three-fourths its volume of the fuming acid to 200° – 245° for three to five hours. The black mass is then dissolved in water and neutralised with calcium carbonate; the calcium salt is converted into the potassium salt; and the solution evaporated. By this means crystals of two kinds are obtained, which must be separated mechanically. One of these, *potassium m-benzenedisulphonate*, $C^6H^3(SO^2K)H(SO^2K)H^2 + H^2O$, forms large, colourless, sharply-defined prisms, very soluble in water, but insoluble in alcohol; whilst the other, *potassium p-benzenedisulphonate*, $C^6H^2(SO^2K)H^2(SO^2K)H^2 + H^2O$, is obtained in ill-defined, thin, iridescent plates, less soluble in water than the

meta-compound. The acids are liberated from the purified potassium salts by adding a considerable excess of sulphuric acid, precipitating the potassium sulphate with alcohol, and finally removing the excess of sulphuric acid with barium hydrate. Both acids are deliquescent, crystalline substances, closely resembling each other.

Derivatives of p-Benzenedisulphonic Acid. — The barium salt, $C^6SO^2.H.H.SO^2.H^2 + H^2O$, forms crystalline crusts, consisting of microscopic needles, — Ba —

much less soluble in water than the corresponding *m*-compound. The lead salt, $C^6SO^2.H.H.SO^2.H^2 + H^2O$, forms small, granular crystals, which under the microscope — Pb —

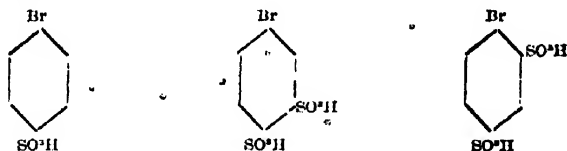
are resolved into nodules of minute needles. This is also somewhat less soluble than the α -compound.

The chloride, $C^6SO^2.Cl.H.H.SO^2.Cl.H^2$, obtained by the action of PCl^3 on the potassium salt, crystallises in long transparent needles melting at 131° . The amide, $C^6SO^2.NH^2.H.H.SO^2.NH^2.H^2$, crystallises from water in very thin scales, and from alcohol in plates which melt at 288° .

The chloride, treated with tin and hydrochloric acid, is converted into thiohydroquinone, $C^6H^4S^2$, which sublimes in lustrous hexagonal plates; and the potassium salt, distilled with potassium cyanide, yields a dicyanobenzene, $C^6H^4(CN)^2$, which, when boiled with caustic alkali, is converted into terephthalic acid. These two reactions^a show that the acid under consideration is the para-acid (Körner a. Monselise).

Benzenemetadisulphonic Acid, $C^6.SO^2.H.H.SO^2.H.H^2$, may be prepared by the following processes:—

(a.) By treating parabromobenzenesulphonic acid with strong sulphuric acid, whereby it is converted into a bromobenzenedisulphonic acid, which must be either the ortho- or the meta-modification:



and debrominating the lead or barium salt of this acid by the action of sodium-amalgam. The amalgam is gradually added to an aqueous solution of the salt, heated to 40° – 45° , and neutralised from time to time with hydrochloric or sulphuric acid. When the action is complete, the excess of alkali is exactly neutralised, and the liquid evaporated to the crystallising point. Chloride or sulphate of sodium then separates out, and afterwards the benzenedisulphonate, still, however, contaminated with inorganic salts.

On heating the benzenedisulphonate thus obtained with potassium ferrocyanide, a crystalline cyanide is obtained, and this, when saponified by prolonged boiling with alcoholic potash in a flask with reversed condenser, is converted into a potassium salt, which, when decomposed by hydrochloric acid, yields isophthalic acid. Consequently, the benzenesulphonic acid obtained as above is metabenzenedisulphonic acid, $C^6.SO^2.H.H.SO^2.H.H^2$. The sodium salt of this acid, fused with potassium hydrate, yields resorcin (Nörling, *Deut. Chem. Ges. Ber.* viii, 1110).

(b.) By heating benzenemonosulphonic acid with an equal weight of fuming sulphuric acid, till white fumes begin to appear, dissolving the resulting brown mass in water, saturating the solution with lead carbonate, and decomposing the resulting lead salt, after filtration from lead sulphate, with hydrogen sulphide. The acid thus obtained may be purified by converting it into the potassium salt, and decomposing this salt with the requisite quantity of sulphuric acid (Barth a. Senhofer, *Deut. Chem. Ges. Ber.* viii, 147).

According to Heinzelmann (*Liebig's Annalen*, clxxxviii, 169), the best mode of proceeding is to dissolve benzene in a retort in an equal volume of fuming sulphuric acid, then add another equal quantity of the same acid, and heat the retort, with its beak inclined upwards, for two or three hours, strongly enough to fill it with white vapours, but not to cause these vapours to escape. The thick dark-coloured mass thus obtained is dissolved in water, saturated with calcium hydrate, and strained; and if the liquid which runs through is very dark-coloured, part of it, after precipitation of the lime with sulphuric acid, is boiled with lead carbonate, the solution of the lead salt is added to the rest of the calcium benzenedisulphonate, and hydrogen

sulphide is passed through the liquid. The lead sulphide thereby precipitated c down the colouring matters; and the colourless filtrate, freed from lime by precipitation with potassium carbonate, yields on evaporation fine crystals of potassium benzenedisulphonate. For further purification, the potassium salt may be converted into the chloride, and the acid regenerated therefrom.

(c.) From the dinitrobenzenedisulphonic acid, $C^6H^2(NO^2)_2(SO^3H)^2$, formed by the action of a mixture of strong nitric and sulphuric acids on metanitrobenzenesulphonic acid (p. 223). This dinitro-acid is reduced by tin and hydrochloric acid to the corresponding diamido-acid, and the latter by nitrous acid to the azo-compound, $C^6H^2\{N^2\}(SO^3)^2$, which, when boiled with absolute alcohol under pressure, is converted into benzenemetadisulphonic acid (Limpricht, *Deut. Chem. Ges. Ber.* viii. 189).

Benzenemetadisulphonic acid crystallises with difficulty, and is extremely deliquescent. Dried at 100° , it has the composition $C^6H^2(SO^3H)^2 + 2\frac{1}{2}H^2O$, and gives off 2 mols. water at 130° . The potassium salt, $C^6H^2(SO^3K)^2 + H^2O$, crystallises in large oblique four-sided prisms easily soluble in water, and gives off its water of crystallisation at 230° . The barium, calcium, copper, lead, and zinc salts, formed by neutralising the acid with the respective carbonates, all contain water of crystallisation, which they give off at high temperatures, and are all freely soluble in water. The silver salt is anhydrous (Barth a. Senhofer).

The barium salt, $C^6(SO^3H)(SO^3H)^2 + 2H^2O$, crystallises from a dilute solution in Ba .

large, colourless prisms, which are sometimes quite transparent, whilst from a concentrated solution it separates in nodules consisting of colourless needles. The lead salt, $C^6(SO^3H)(SO^3H)^2 + 2H^2O$, appears to be isomorphous with the barium salt. The Pb .

copper salt, $C^6(SO^3H)(SO^3H)^2 + 6H^2O$, forms blue needles; the sodium salt, $C^6(SO^3Na)(SO^3Na)^2 + 4H^2O$, crystallises in colourless needles, and the cadmium salt in small colourless prisms (Körner a. Monselise).

The chloride, $C^6SO^2Cl.H.SO^2Cl.H^2$, crystallises from ether in large colourless prisms melting at 63° ; the amide, $C^6SO^2NH^2.M.SO^2NH^2.H^2$, in needles resembling sublimed benzoic acid, and melting at 229° .

The chloride treated with tin and hydrochloric acid yields thioresorcin, and the dicyanobenzene obtained by distilling the potassium salt with potassium cyanide is converted by boiling with potash into isophthalic acid.

Derivatives of Benzenemetadisulphonic Acid (Heinzelmann, *Liebig's Annalen*, clxxxviii. 160). This acid yields two series of mono-substitution-derivatives, which may be distinguished as α and β .

The nitrobenzenedisulphonic acids, $C^6H^2(NO^2)(SO^3H)^2$, are obtained by gradually adding 2 vols. of the strongest nitric acid to 1 vol. of the dehydrated benzenedisulphonic acid contained in a tubulated retort, and keeping the mixture for eight or ten hours in a state of gentle ebullition, the acid which distils over being poured back from time to time. When the action is over, the excess of nitric acid is driven off on the water-bath, the residue is dissolved in water, and the solution neutralised with barium carbonate and evaporated. The first crystallisations consist of needles of the barium salt of the α -acid; the next of these needles mixed with nodules of the β -salt; and the last crystallisations of the nodules only. These salts must be separated as completely as possible by mechanical selection, and then purified by recrystallisation.

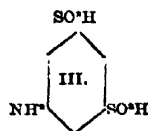
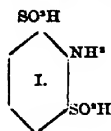
By decomposing the purified barium salts with sulphuric acid, and evaporating the filtered solutions to a syrupy consistence, the α -acid is obtained in long slender deliquescent needles; the β -acid, after long standing over sulphuric acid, in small very hygroscopic crystals. All the salts of these acids are very soluble in water, those of the β -acid being the more soluble of the two.

The amidobenzenemetadisulphonic acids, α and β , $C^6H^2(NH^2)(SO^3H)^2$, are formed from the corresponding nitro-acids by passing hydrogen sulphide through their ammoniacal solutions. The liquid filtered from sulphur is evaporated to expel the ammonium sulphide, then boiled with baryta-water till all the ammonia is driven off, and the barium is precipitated by sulphuric acid. The free acids thus obtained are separated by boiling the solution with lead carbonate, whereby the α -acid is completely, the β -acid only half precipitated; the salts which separate out on evaporation (the neutral α - and the acid β -salt) are purified by recrystallisation; and from these salts the acids are obtained by means of hydrogen sulphide.

The α -acid crystallises from very concentrated solutions in colourless thick four

and six-sided prisms containing 3 mols. H^2O , which they do not give off either in the air or over sulphuric acid. It dissolves easily in water and alcohol, and is precipitated from the alcoholic solution by ether. The β -acid separates from a solution evaporated to a syrup, and left over sulphuric acid, in nodular groups of brownish microscopic needles containing $2\frac{1}{2}H^2O$, easily soluble in water and in alcohol, decomposing above 120° .

The aqueous solution of the α -acid gives with bromine-water a precipitate of bromanil, $C^6H^3Br^3O^2$; that of the β -acid, treated in like manner, yields a copious precipitate of ordinary tribromaniline. From these reactions the constitution of the α and β amido-derivatives—and hence that of the nitro-derivatives—may be inferred, at least with great probability. The derivatives of these two series being both formed from benzenemetadisulphonic acid, the only possible formulae by which they can be represented are the three following:—



Now the experiments of Berndsen and Beckurts on the amidobenzenesulphonic acids, $C^6H^4NH^2SO^3H$ (p. 226), have shown that the ortho- and para-compounds treated with excess of bromine yield tribromaniline, whereas the meta-compound yields bromanil. Hence it may be inferred, as most probable, that the α -amidobenzenedisulphonic acid, which is converted by bromine into bromanil, has the constitution represented by the figure III., in which both the SO^3H -groups are in the meta-position with respect to the NH^2 .

The β -amidobenzenedisulphonic acid, on the other hand, is converted by excess of bromine into tribromaniline ($NH^2 : Br : Br : Br :: 1 : 2 : 4 : 6$), which might be formed, without any transposition of atoms, from either of the compounds I or II, by exchange of the two SO^3H -groups and of 1 at. H for bromine. Of these two formulae Heinzelmann gives the preference to II, which is that of Hofmann's disulphanilic acid (formed by the action of fuming sulphuric acid on sulphanilic [*p*-amidobenzenesulphonic] acid, and converted by exchange of NH^2 for H into *meta*-amidobenzenedisulphonic acid), inasmuch as disulphanilic acid is also converted by excess of bromine into ordinary tribromaniline, and resembles the β -amidobenzenedisulphonic acid in other respects.

Diazo-derivatives, $C^6H^3N^2(SO^3H)^2$.—These acids are formed by passing nitrous acid through the solutions of the amido-acids in strong alcohol, and are precipitated from their alcoholic solutions by ether in the form of oily liquids, which solidify over sulphuric acid, the α -acid to a crystalline pulp of slender needles, the β -acid in small nodules which absorb moisture from the air and decompose.

The neutral salts of these acids have not been obtained: the acid salts, $C^6H^3N^2(SO^3M)(SO^3H)$, are produced by the action of nitrous acid on the acid salts of the corresponding amido-acids. They mostly crystallise well, and swell up strongly when heated on platinum foil, leaving a difficultly combustible cinder. The α and β salts are distinguished chiefly by their crystalline forms.

These diazo-acids appear to have the constitution represented by the formula $C^6H^3 \begin{matrix} SO^3H \\ \diagup \\ N=N \\ \diagdown \\ SO^3H \end{matrix}$, derived from that of the amido-acids, $C^6H^4 \begin{matrix} SO^3H \\ \diagup \\ NH^2 \\ \diagdown \\ SO^3H \end{matrix}$, by substitution of a trivalent nitrogen-atom for the 2 at. hydrogen of the NH^2 and 1 at. of hydrogen from the benzene-residue, C^6H^3 , the other nitrogen-atom becoming quinquivalent.

The following table gives a comparative view of the principal properties of the salts, chlorides, and amides of the nitro-, amido-, and diazo-derivatives of the α and β series:

Derivatives of Benzene-m-disulphonic acid.

Nitro-derivatives:

$C^6H^4(NO^2)(SO^3H)^2 + xH^2O$.	Slender, deliquescent needles, very soluble in water.	Small, very hygroscopic crystals, more soluble than α .
$C^6H^4(NO^2)(SO^3NH^2)^2$ (anhydr.)	Yellowish flat prisms, with oblique end-face.	Nodules and crusts of small prisms.

Derivatives of Benzene-m-disulphonic acid.—Continued.*Nitro-derivatives :*

$\text{C}^6\text{H}^4(\text{NO}^2)(\text{SO}^2\text{K})^2$.	Anhydrous, slender needles, somewhat less soluble than the barium salt.	$+ \frac{1}{2}\text{H}^2\text{O}$ (?) Nodular groups of slender microscopic needles.
$\text{C}^6\text{H}^4(\text{NO}^2)(\text{SO}^2\text{Ag})^2$	White nodules, easily soluble, blackened by light.	
$\text{C}^6\text{H}^4(\text{NO}^2)(\text{SO}^2)^2\text{Ba}$.	Slender needles with $5\text{H}^2\text{O}$; after recrystallisation, flat shining efflorescent prisms, with $6\text{H}^2\text{O}$ and $4\text{H}^2\text{O}$.	Nodular groups of slender needles, with $5\text{H}^2\text{O}$, turning yellow in light without losing water.
$\text{C}^6\text{H}^4(\text{NO}^2)(\text{SO}^2)^2\text{Ca}$.	$+ 2\text{H}^2\text{O}$. Yellow (monoclinic) (?) prisms, which quickly effloresce.	
$\text{C}^6\text{H}^4(\text{NO}^2)(\text{SO}^2)^2\text{Pb}$.	$+ 4\text{H}^2\text{O}$. Nearly colourless, slender, very soluble needles.	$+ 4\text{H}^2\text{O}$. Highly concentrated solution solidifies to a pulp of slender needles; weaker solution left to evaporate effloresces very strongly.
$\text{C}^6\text{H}^4(\text{NO}^2)(\text{SO}^2\text{Cl})^2$.	Melts at 140° .	Brown oil, not solidifying in a freezing mixture.
$\text{C}^6\text{H}^4(\text{NO}^2)(\text{SO}^2\text{NH}^2)^2$	Nacreous, microscopic, three-sided laminæ, melting at 242° .	

Amido-derivatives :

$\text{C}^6\text{H}^4(\text{NH}^2)(\text{SO}^2\text{H})^2$.	$+ 3\text{H}^2\text{O}$. Four- and six-sided prisms, very soluble in water and alcohol. With bromine water gives bromanil.	$+ 2\frac{1}{2}\text{H}^2\text{O}$. Brownish nodular groups of microscopic needles, very soluble in water and alcohol. With bromine-water gives (1 : 2 : 4 : 6), tribromaniline.
$\text{C}^6\text{H}^4(\text{NH}^2)(\text{SO}^2\text{NH}^2)^2$	$+ \text{H}^2\text{O}$. Large, six-sided laminæ, very soluble in water and alcohol.	
$\text{C}^6\text{H}^4(\text{NH}^2)\left\{\begin{smallmatrix}\text{SO}^2\text{NH}^2 \\ \text{SO}^2\text{H}\end{smallmatrix}\right.$	$+ x\text{H}^2\text{O}$. Flat anhydrous prisms or long hydrated needles, quickly efflorescing.	
$\text{C}^6\text{H}^4(\text{NH}^2)(\text{SO}^2\text{K})^2$.	Long, flat, non-efflorescent prisms with $4\text{H}^2\text{O}$, or quickly efflorescing rhombic octohedrons with $3\text{H}^2\text{O}$.	
$\text{C}^6\text{H}^4(\text{NH}^2)\left\{\begin{smallmatrix}\text{SO}^2\text{H} \\ \text{SO}^2\text{K}\end{smallmatrix}\right.$.	$+ \text{H}^2\text{O}$. Long prisms, or thicker flat prisms, with oblique end-face, moderately soluble in cold water.	
$\text{C}^6\text{H}^4(\text{NH}^2)(\text{SO}^2)^2\text{Ba}$	$+ 3\frac{1}{2}\text{H}^2\text{O}$. Concentric groups of long thin prisms, easily soluble in water; precipitated amorphous by alcohol.	$+ 3\text{H}^2\text{O}$. Concentric groups of brownish four-sided tablets.

Derivatives of Benzene-m-disulphonic acid.—Continued.

Amido-derivatives :

β

$[C^6H^4(NH^2)(SO^3H)SO^3]^2Ba$	+ 5H ² O. Long thin prisms, moderately soluble in cold water.	+ 2H ² O. Separates from hot concentrated solution as a bulky mass of slender shining microscopic needles, slowly re-dissolving in water.
$C^6H^4(NH^2)(SO^3)^2Pb$	+ 3½H ² O. Large six-sided prisms, rather sparingly soluble in cold water.	+ 2H ² O. Hard crusts made up of nodules.
$[C^6H^4(NH^2)(SO^3H)SO^3]^2.Pb$	+ 6H ² O. Tufts of colourless prisms.	+ 6H ² O. Small, colourless, shining, pointed rhombic tablets, united in crusts. Dissolves very slowly in cold water.
$C^6H^4(NH^2)(SO^3Ag)^2$	(anhydr.) Colourless or faintly reddish rhombic tablets, scarcely coloured by light, slightly soluble in water.	

Diazo-derivatives :

$C^6H^4N^2(SO^3H)^2$	Precipitated from alcoholic solution by ether as a brown oil, solidifying over sulphuric acid to a pulp of small needles; very soluble in water and alcohol (p. 253).	Solidifies over sulphuric acid to small nodules, which absorb moisture from the air and decompose.
$C^6H^4N^2 \begin{cases} SO^3H \\ SO^3NH^4 \end{cases}$	Anhydrous. Concentric groups of white needles.	
$C^6H^4N^2 \begin{cases} SO^3H \\ SO^3K \end{cases}$	Anhydrous. Faintly reddish needles.	Anhydrous. Slender microscopic prisms, burning away quickly on platinum foil, and leaving a light spongy mass.
$[C^6H^4N^2(SO^3H)SO^3]^2Ba$	+ 3H ² O. Nearly colourless, shining, microscopic four-sided plates.	+ 2H ² O. Concentric groups of short monoclinic prisms.
$[C^6H^4N^2(SO^3H)SO^3]^2Pb$	+ 3H ² O. Flat microscopic prisms.	+ 3H ² O. Thin, microscopic needles.

Bromobenzenedisulphonic Acids, $C^6H^4Br(SO^3H)^2$. These acids are formed by heating the above-described diazobenzenedisulphonic acids with hydrobromic acid: only the α-compounds have, however, as yet been investigated.

The free acid, purified by converting it into a lead salt, frequently recrystallising this salt, and then decomposing it with hydrogen sulphide, crystallises from its syrupy solution, after standing for several days over sulphuric acid, in slender colourless needles which are too hygroscopic to admit of a determination of their water of crystallisation.

The metallic bromobenzenedisulphonates are obtained by treating the acid salts of α-diazobenzenedisulphonic acid with hydrobromic acid.

$C^6H^4Br(SO^3NH^4)^2$. Concentric groups of anhydrous, slender, easily soluble

$C^6H^3Br(SO^2K)^2 + 4H^2O$ (?). Slender very soluble needles, which effloresce quickly on exposure to the air.

$C^6H^3Br(SO^2)^2Ba + 2\frac{1}{2}H^2O$. Nearly colourless needles, easily soluble in water.

$C^6H^3Br(SO^2)^2Pb + 2\frac{1}{2}H^2O$. Thin colourless prisms, easily soluble in water.

Chloride, $C^6H^3Br(SO^2Cl)^2$. Crystallises from ether in crusts made up of white nodules, somewhat sparingly soluble in ether. Melts at 99° .

Amide, $C^6H^3Br(SO^2NH^2)^2$. White silky needles nearly insoluble in cold, more easily soluble in hot water, melting at 245° .

Bromamidobenzenedisulphonic Acids. Of these also only the α -modifications have been studied. On adding bromine to a cold dilute aqueous solution of α -amidobenzenedisulphonic acid, the colour of the bromine disappears, and if only 1 mol. bromine is added, the solution contains mono- and dibromamidobenzenedisulphonic acid, together with unaltered amido-acid; if 2 or more mols. of bromine are added, the dibrominated acid which separates is accompanied by shining laminae of bromanil, the quantity of which increases in direct proportion to the bromine added.

To separate these acids, the solution of the amidobenzenedisulphonic acid, mixed with 1 mol. bromine, is evaporated on the water-bath till all the hydrobromic acid is removed, and the syrupy residue is left for several days over sulphuric acid, whereupon thick crystals of the unaltered amido-acid first separate out, after which the mother-liquor gradually solidifies, from separation of nodular groups of needles. These nodules, heated with water and barium carbonate, yield a barium salt which crystallises in similar forms, and may be converted into the ammonium salt by treatment with ammonium carbonate. The moderately concentrated solution of the ammonium salt thus obtained deposits: first, nearly colourless dense prisms, or square plates of ammonium α -ditromamidobenzenedisulphonate; the mother-liquor of these yields large yellow prisms of the α -monobromamidobenzenedisulphonate, and the last mother-liquor yields the α -amidobenzenedisulphonate. The several kinds of crystals thus obtained must be purified by repeated crystallisation.

When the solution of the amido-acid is mixed with more than 1 mol. bromine, the mode of treatment is essentially the same, excepting that the barium salt must be prepared by boiling the nodular crystals with baryta-water, in order to remove ammonium sulphate, which is formed together with the bromanil.

Bromamidobenzenedisulphonic acid, $C^6H^2Br(NH^2)(SO^2H)^2 + 2\frac{1}{2}H^2O$, separated from the lead salt by hydrogen sulphide, forms thick colourless prisms, very soluble in water.

$C^6H^2Br(NH^2)(SO^2NH^2)^2$ (anhydrous?), forms large, nearly colourless prisms, apparently containing mechanically enclosed water (up to 3 per cent.), and therefore decrepitating when heated.

$C^6H^2Br(NH^2)(SO^2)^2Ba + 8H^2O$, separates from the syrupy solution in spherical groups of slender needles, efflorescing on exposure to the air.

$C^6H^2Br(NH^2)(SO^2)^2Pb + 3H^2O$ separates from the syrupy solution in nearly colourless hard nodules, composed of slender prisms, which redissolve but slowly in cold water and do not effloresce in the air.

Dibromamidobenzenedisulphonic acid, $C^6HBr^2(NH^2)(SO^2H)^2 + 4H^2O$, crystallises in dense, colourless, non-efflorescent prisms, easily soluble in water.

$C^6HBr^2(NH^2)(SO^2NH^2)^2$ (anhydrous). Dense, colourless prisms or square tables, somewhat sparingly soluble in cold water.

$C^6HBr^2(NH^2)(SO^2K)^2$ (anhydrous). Dense, colourless prisms, more soluble than the ammonium salt.

$C^6HBr^2(NH^2)(SO^2)^2Ba + 8H^2O$. Long, thin, colourless prisms, very soluble in water, and efflorescing quickly on exposure to the air.

$C^6HBr^2(NH^2)(SO^2)^2Pb + 3H^2O$. Thin, flat, non-efflorescent prisms, separating from the syrupy solution after standing for several days.

Acid Potassium Dibromodiazobenzenedisulphonate, $C^6Br^2N^2 \begin{smallmatrix} SO^2H \\ SO^2K \end{smallmatrix}$, is formed by passing nitrous acid into a solution of dibromamidobenzenedisulphonic acid half neutralised with potassium carbonate, and separates in anhydrous, microscopic, six-sided rhombic tablets. It is easily decomposed by boiling with water or alcohol, but more easily by heating with concentrated hydrobromic acid, yielding:

Potassium Tribromobenzenedisulphonate, $C^6HBr^3(SO^2K)^2$, which crystallises in small anhydrous prisms, somewhat sparingly soluble in water (Heintzelmann).

The following table gives a synoptic view of the derivatives of benzenesulphonic acid above described:—

BENZENESULPHONIC ACIDS.

Abbreviated symbol of compound	Melting point of		Position of the displacing radicles relatively to the SO ² H-group, which occupies position 1				
	Chloride	Amide	Ortho 2	Meta 3	Para 4	Meta 5	Ortho 6
Br	51°	186°	Br	—	—	—	—
Br	liquid	153°-154°	—	Br	—	—	—
Br	76°	160°	—	—	Br	—	—
Br.Br	71°	193°	Br	—	—	Br	—
Br.Br	57.5°	203°	—	Br	—	Br	—
Br.Br	31°	170°	—	Br	Br	—	—
Br.Br	127°	215°	Br	Br	—	—	—
Br.Br.Br	127°	210°	—	Br	Br	Br	—
Br.Br.Br	85.5°	blackens at 220°	Br	Br	—	Br	—
Br.Br.Br	63°	blackens at 210°	Br	—	Br	—	Br
Br.Br.Br	64.5°	228°	Br	—	—	Br	Br
Br.Br.Br.Br	120°	181°	Br	Br	Br	Br	—
Br.Br.Br.Br	91°	blackens at 250°	Br	Br	Br	—	Br
Br.Br.Br.Br	91.5°	above 300°	Br	Br	—	Br	Br
Br.Br.Br.Br.Br	90°	blackens at 250°	Br	Br	Br	Br	Br
Cl	28.5°	188°	Cl	—	—	—	—
Cl	liquid	148°	—	Cl	—	—	—
Cl	53°	143°-144°	—	—	Cl	—	—
I	51°	170°	I	—	—	—	—
NO ²	67°	186°	NO ²	—	—	—	—
NO ²	61°	161°	—	NO ²	—	—	—
NO ²	liquid	131°	—	—	NO ²	—	—
NO ² .NO ²	89°	238°	NO ²	NO ²	—	—	—
NO ² .Br	42°	205°	Br	—	—	NO ²	—
NO ² .Br.Br	121°	—	NO ²	Br	—	Br	—
NO ² .Br.Br.Br	116°	202°	NO ²	Br	Br	Br	—
NO ² .Br.Br.Br	turns brown at 180°	turns brown at 210°	Br	NO ²	Br	—	Br
NO ² .Br.Br.Br.Br	142°	175°	Br	NO ²	—	Br	Br
NO ² .Br.Br.Br.Br	146°-147°	above 300°	Br	Br	NO ²	Br	Br
Characters of free acid							
NH ²	Anhydr. rhombs, or prisms with 1H ² O		NH ²	—	—	—	—
NH ²	Anhydr. needles, or prisms with 1.5H ² O		—	NH ²	—	—	—
NH ²	Rhombic plates with 1H ² O		—	—	NH ²	—	—
NH ² .NH ²	Rhombic prisms		NH ²	NH ²	—	—	—
NH ² .Br	Crystalline powder, 1H ² O		—	NH ²	Br	—	—
NH ² .Br	Needles with 1H ² O		—	NH ²	—	—	Br
NH ² .Br.Br	Prisms or tables with 1H ² O		NH ²	Br	—	Br	—
NH ² .Br.Br	Needles		Br	NH ²	—	Br	—
NH ² .Br.Br	Prisms		or Br	Br	NH ²	NH ²	—
NH ² .Br.Br.Br	Needles		—	Br	NH ²	Br	—
NH ² .Br.Br.Br	"		NH ²	Br	Br	Br	—
NH ² .Br.Br.Br	"		Br	NH ²	—	—	Br
NH ² .Br.Br.Br.Br	"		Br	NH ²	—	Br	Br
NH ² .Br.Br.Br.Br	"		Br	Br	NH ²	Br	Br
Melting point of							
Bensedisulphonic acids	Chloride	Amide					
SO ² H	131°	288°	—	—	SO ² H	—	—
SO ² H	63°	229°	—	SO ² H	—	—	—
α. SO ² H.Br	99°	245°	—	SO ² H	—	Br	—
α. SO ² H.NO ²	140°	242°	—	SO ² H	—	NO ²	—
β. SO ² H.NO ²	oil	—	—	SO ² H	NO ²	—	—
α. SO ² H.NH ²	Prisms with 3H ² O		—	SO ² H	—	NH ²	—
β. SO ² H.NH ²	Needles with 2½H ² O		—	SO ² H	NH ²	—	—

Disulphonic Acid, $C^6H^4(NO_2^2)(SO^2H)^2$ (Limpricht, *Deut. Chem. Ges. Ber.* viii. 289). This acid is produced by boiling ordinary (meta) nitrobenzenesulphonic acid with half its volume of strong sulphuric acid and three times its volume of nitric acid, sp. gr. 1.5. When separated from its lead salt, it solidifies on standing to a crystalline mass having a very bitter taste. Its salts are very soluble and do not crystallise very readily. The following have been examined:—

$2(NO_2^2)(SO^2K)^2 + H^2O$. White needles.

$2(SO^2Na)^2 + 3H^2O$. Long needles.

a + $2H^2O$. Slender needles grouped in tufts.

a + H^2O . Stellate groups of prisms.

b + $3H^2O$. Crystalline crusts.

1 + $3H^2O$. Stellate groups of microscopic crystals.

The chloride, $C^6H^4(NO_2^2)(SO^2Cl)^2$, crystallises in oblique four-sided tables; the amide in long needles: both compounds when heated decompose without melting.

Nitramidobenzenedisulphonic acid, formed by reducing the dinitro-acid with ammonium sulphide, is a very deliquescent mass, very difficult to crystallise, and forming deliquescent salts. The *barium salt*, $C^6H^4(NO^2)(NH^2)(SO^2Ba) + 2H^2O$, is precipitated from its aqueous solution by alcohol in the crystalline state.

This amido-acid, dissolved in absolute alcohol and treated with nitrous acid, yields the diazo-compound, $C^6H^4(NO^2) \begin{array}{c} \diagup N \\ \text{---} SO^2 \text{---} N \\ \diagdown SO^2 H \end{array}$, which separates in red flakes. The

same amido-acid, boiled with absolute alcohol, is converted into uncrystallisable nitrobenzenedisulphonic acid, the lead salt of which, $C^6H^4(NO^2)(SO^2Pb) + H^2O$, crystallises in tufts of yellow needles.

The diazo-compound, boiled with water, yields nitrodiphenol-disulphonic acid, which crystallises in very soluble microscopic needles; and forms a barium salt, $C^6H^4(NO^2)(OH)(SO^2Ba) + 2H^2O$, which is precipitated from aqueous solution by alcohol in the crystalline state.

Nitrobromobenzenedisulphonic acid, $C^6H^3(NO^2)Br(SO^2H)^2 + H^2O$, formed by heating the diazo-compound with hydrobromic acid, crystallises in rhombic plates, easily soluble in water and in alcohol, and forms uncrystallisable salts with ammonium, barium and lead.

Diamidobenzenedisulphonic acid, $C^6H^4(NH^2)^2(SO^2H)^2 + H^2O$, obtained by the reducing action of tin and hydrochloric acid on the dinitro-acid, crystallises in easily soluble quadratic octahedrons; its *tin-salt*, $C^6H^4(NH^2)^2(SO^2Sn) + H^2O$, crystallises in white needles.

The diamido-acid, distilled with soda-lime, is converted into metaphenylenediamine, $C^6H^4NH^2.H.NH^2.H$, melting at 60° . The same acid, suspended in absolute alcohol and decomposed by nitrous acid, is converted into the azo-compound,

2 , a yellow crystalline powder, which, when boiled with absolute alcohol under pressure, yields benzenedisulphonic acid (p. 251).

Dihydroxybenzenedisulphonic acid, $C^6H^4(OH)^2(SO^2H)^2$, obtained by boiling the azo-compound just mentioned with water, crystallises in long four-sided easily soluble needles. Its *barium salt*, $C^6H^4(OH)^2(SO^2Ba) + 2H^2O$, is precipitated in the crystalline form from its aqueous solution by alcohol (Limpricht).

Dibromobenzenedisulphonic acid, $C^6H^2Br^2(SO^2H)^2$, obtained by treating the same azo-compound with hydrobromic acid, is very deliquescent, and does not yield crystallisable salts (Limpricht).

In this, as in the preceding disubstituted derivatives of benzene-*m*-disulphonic acid, the relative position of the two bromine-atoms is not known.

Another dibromobenzenedisulphonic acid, in which the two Br-atoms are in the para-position with regard to one another, but the places of the two SO^2H -groups are unknown, is formed, together with paradibromobenzenemonosulphonic acid (p. 237) by the action of fuming sulphuric acid on crystallised paradibromobenzene. It crystallises in small, transparent, easily soluble prisms. Its *potassium salt*, $C^6H^2Br^2(SO^2K)^2$, forms white soluble needles. The *barium salt*, $C^6H^2Br^2(SO^2Ba) + 4\frac{1}{2}H^2O$, crystallises in small white easily soluble needles. The *chloride*, $C^6H^2Br^2(SO^2Cl)^2$, forms transparent monoclinic crystals melting at 161° . The *amide*, $C^6H^2Br^2(SO^2NH^2)^2$, forms nodules of microscopic needles, easily soluble in water and in alcohol. It does not melt at 240° , but melts and turns brown when strongly heated on platinum foil (Borns, *Liebig's Annalen*, cxxxvii. 366).

This dibrominated acid, boiled with strong nitric acid, is converted into a nitro-dibromobenzenedisulphonic acid, which is easily reduced by tin and hydrochloric acid to the corresponding amidodibromobenzenedisulphonic acid,

$\text{O}^-\text{HBr}^+(\text{NH}^+(\text{SO}^-\text{H})^2)$, which forms small crystals easily soluble in water and in alcohol. Its potassium and barium salts are crystalline and easily soluble. The chloride crystallises in prisms melting at 148° ; the amide forms small needles melting at 206° (Borns).

Benzenetrisulphonic Acid, $\text{C}^6\text{H}^3(\text{SO}^-\text{H})^3$. This acid is obtained by dissolving 10 grams of benzene in 70 grams of well-cooled oil of vitriol, mixing the liquid quickly with 35–40 grams of phosphorus pentoxide, and then heating the viscous solution for five to six hours to 280° – 290° . The product is boiled with water, and milk of lime is added until the solution is alkaline. The filtrate is then neutralised at 100° with acid potassium carbonate, and normal carbonate is added as long as a precipitate is formed. On evaporating the filtrate, potassium benzenetrisulphonate crystallises out and may be purified by recrystallisation: it forms large oblique prisms or plates, consisting of $\text{C}^6\text{H}^3(\text{SO}^-\text{K})^3 + 3\text{H}_2\text{O}$. To obtain the free acid, a solution of this salt is mixed with lead acetate, and the liquid precipitated by ammonia. After washing, the precipitate is decomposed by hydrogen sulphide. On evaporating the solution, benzenetrisulphonic acid, $\text{C}^6\text{H}^3(\text{SO}^-\text{H})^3 + 3\text{H}_2\text{O}$, crystallises in long flat deliquescent needles. The barium salt, $[\text{C}^6\text{H}^3(\text{SO}^-\text{H})^3]_2\text{Ba}^2$, is a crystalline precipitate which is sparingly soluble in water and almost insoluble in dilute alcohol; by the slow evaporation of its aqueous solution it is obtained in very small needles. The silver salt, $\text{C}^6\text{H}^3(\text{SO}^-\text{Ag})^3 + 2\text{H}_2\text{O}$, is obtained by boiling the acid with freshly precipitated silver oxide; on evaporating the solution in a vacuum it crystallises in well-defined needles. The lead salt, $[\text{C}^6\text{H}^3(\text{SO}^-\text{H})^3]_2\text{Pb}^2 + 4\text{H}_2\text{O}$, is readily soluble in water, and crystallises in slender needles. The cadmium salt forms small plates, and dissolves freely in water (Senhofer, *Liebig's Annalen*, clixiv. 243).

BENZHYDROXAMIC ETHERS. See HYDROXAMIC ETHERS.

BENZHYDRYL-BENZOIC ACID. See BENZOYL-BENZOIC ACID.

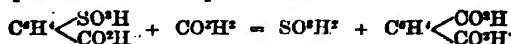
BENZOIC ACID, $\text{C}^6\text{H}^5\text{COOH}$. Guichard (*Bull. Soc. Chim.* [2], xix. 351) has observed the formation of large crystals of benzoic acid in carbon bisulphide which had been for a long time in contact with gum benzoïn at varying temperatures.

Lithium Benzoate, $\text{C}^6\text{H}^5\text{CO}^-\text{Li}^+$, easily prepared by boiling the carbonate with water (9 pts.) and gradually adding benzoic acid (about $3\frac{1}{2}$ pts.), crystallises in shining laminae, greasy to the touch, and having a sweet, not unpleasant taste. It dissolves in $3\frac{1}{2}$ pts. water at 16° , in $2\frac{1}{2}$ pts. at 100° , and in 10 pts. cold alcohol of sp. gr. 0.836. The solution has an acid reaction (E. B. Shuttleworth, *Pharm. J. Trans.* [3], v. 682).

Reactions.—1. With *Glucose and Sulphuric acid*.—According to Phipson (*Chem. News*, xxviii. 13) benzoic [or salicylic] acid (3 mols.) gently heated with glucose (1 mol.) and an excess of strong sulphuric acid, forms a solution of a fine blood-red colour, which after a while turns brown, and then black. A similar observation has been made by Kingzett & Hake (*ibid.* xxxv. 37).

2. With *Ethyl Nitrate and Sulphuric Acid*.—When a solution of equal numbers of molecules of benzoic acid and ethyl nitrate in pure ether is added to concentrated sulphuric acid, at a temperature not exceeding 75° , a little metanitrobenzoic acid is formed, together with a large quantity of ethyl benzoate and a liquid boiling at 270° – 280° . This liquid is decomposed by potash, yielding an acid melting at 136° – 137° , and consisting of a compound of benzoic acid and a nitrobenzoic acid, which melts at 128° – 130° (Fittica, *Deut. Chem. Ges. Ber.* ix. 794).

3. With *Sodium Formate*.—V. Meyer showed some time ago (*2nd Suppl.* 134) that potassium sulphobenzoate (or bromobenzoate), heated with sodium formate, is converted into the potassium salt of isophthalic acid:



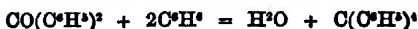
Now, V. v. Richter has since observed (*Deut. Chem. Ges. Ber.* vi. 876) that when potassium benzoate is fused with sodium formate, both isophthalic and terephthalic acids are produced, the former constituting the larger portion of the product:



and he supposes that, in Meyer's reaction, the sodium formate is in the first instance resolved by heat into CO^2 and H^2 , and that the hydrogen thus separated exerts a reducing action on the sulphobenzoic or bromobenzoic acid, giving rise to benzoic acid, which is then acted upon by a fresh portion of the formate, producing sometimes a mixture of isophthalic and terephthalic acid, sometimes isophthalic acid alone. He finds by experiment that bromobenzoic acid heated with sodium formate does actually yield a mixture of the two dicarbon-acids, a result which could scarcely be obtained if the reaction took place, as Meyer supposes, by simple replacement of Br

by CO^*H . Meyer, on the other hand, finds (*ibid.* 1146) that when a salt of ordinary (meta) sulphobenzoic acid is fused with sodium formate, the product consists of isophthalic acid without a trace of terephthalic; whereas, when parasulphobenzoic acid (discovered by Remsen) is similarly treated, nothing but terephthalic acid is produced. He therefore concludes that the dicarbon-acids are formed directly from the sulphobenzoic acid by substitution of COOH for SO^*H , and not by the action of sodium formate on previously formed benzoate. Meyer also finds that a mixture of sodium formate and potassium benzoate undergoes no change at a temperature which suffices for the complete conversion of the sulphobenzoate into isophthalate. Moreover, it appears from experiments by Conrad that iso- and terephthalic acids are formed by simply heating sodium benzoate to the point of carbonisation, whence it is evident that the production of these acids in the manner observed by Richter has nothing to do with their formation from sulphobenzoic or bromobenzoic acid.

4. *Decomposition of Barium Benzoate by Heat.*—This salt yields by dry distillation a large quantity of a hydrocarbon melting at 145° , which appears to be tetraphenylmethane, $\text{C}(\text{C}^*\text{H}^*)^4$, formed by the mutual action of benzophenone and benzene in the nascent state:

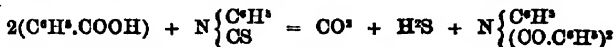


(A. Behr, *Deut. Chem. Ges. Ber.* v. 970).

5. *Reaction with Thiocyanates.*—A mixture of barium benzoate with excess of thiocyanate yields by dry distillation a partially solid distillate, consisting of benzonitril, tolane, and a cyanide of a hydrocarbon, partly liquid, partly solid, neither of which has, however, been obtained pure. The liquid compound, heated with potash, yields benzacrylic acid, $\text{C}^*\text{H}^*.\text{C}.\text{CO}^*\text{H}$ (p. 155). The solid cyano-product yields an acid apparently identical with that which is formed by heating the product of the action of cyanogen on an alcoholic solution of tolane with caustic potash (Pfankuch, *J. pr. Chem.* [2], vi. 113).

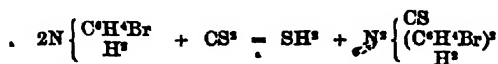
According to Kekulé and Williams (*Deut. Chem. Ges. Ber.* vi. 116), this reaction does not yield benzacrylic acid; but the residues left after the distillation and rectification of the benzonitril (b. p. 191°), yield, on continued distillation under reduced pressure, portions which pass over at 200° – 245° and 245° – 275° , the first of which, when saponified by potash, yields benzoic acid; whilst the higher-boiling portion appears to be a mixture of several hydrocarbons, probably including tolane.

Action of Benzoic Acid on Phenylthiocarbimide (Phenyl Mustard Oil).—These two compounds heated together in sealed tubes to 130° – 150° , yield phenyldibenzamide:

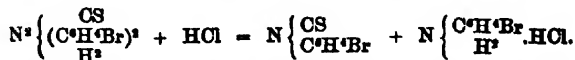


(Lasanitsch, *Deut. Chem. Ges. Ber.* vi. 176).

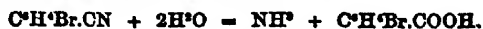
Bromobenzoic Acids. Parabromobenzoic acid, $\text{O}^*.\text{COOH}.\text{H.H}.\text{Br}.\text{H}^*$, produced by oxidation of *p*-bromotoluene (2nd *Suppl.* 161), may also be formed from ordinary bromaniline (m. p. 63° – 64°), by the following series of processes. Bromaniline, prepared by treating acetanilide with bromine and decomposing the resulting bromacetanilide by heating with strong hydrochloric acid, is converted by the action of carbon disulphide in alcoholic solution into the corresponding bromothiocabanilide:



and this compound, heated to 150° – 160° in sealed tubes with strong hydrochloric acid, is resolved into bromophenylthiocarbimide (bromophenyl mustard oil) and bromaniline:



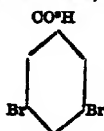
On heating the contents of the tubes with water, the bromophenylthiocarbimide passes over as a colourless oil, which, when heated to 180° – 200° with ignited copper-powder, gives up its sulphur, and is converted into bromophenyl cyanide or bromobenzonitril, $\text{C}^*\text{H}^*.\text{Br}.\text{CN}$, and this nitril heated to about 180° with strong hydrochloric acid, is converted into parabromobenzoic acid:



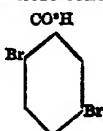
The parabromobenzoic acid thus prepared melts at 250° ; its barium salt crystallises in nacreous laminae (compare 1st *Suppl.* 310). Its formation in the manner above

described shows that ordinary bromaniline^c belongs to the para-series (Weith a. Landolt, *Deut. Chem. Ges. Ber.* viii. 716).

benzoic Acids, $C^6H^3Br^2COOH$. Three of these acids have been obtained, one symmetrical and two unsymmetrical, as represented by the following constitutional formulæ, and a fourth whose constitution is still undetermined :



m. p. 208°-209°



m. p. 151°-152°



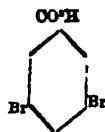
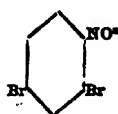
m. p. 227°-230°

(1.) The symmetrical modification, 1 : 3 : 5, is formed by the action of alcoholic potassium cyanide on nitrometadibromobenzene, (1 : 2 : 4), at 120°-140° :



It crystallises from water, in which it is but slightly soluble, in flocks, melts at 208°-209°, and sublimes in flat needles. Its barium salt, $(C^6H^3Br^2)^2Ba$, anhydrous, after drying over sulphuric acid, is very slightly soluble even in hot water, and crystallises in concentric groups of slender needles (V. v. Richter, *Deut. Chem. Ges. Ber.* vii. 1418).

In the formation of this modification, the radicle CO^2H does not occupy the same place relatively to the two bromine-atoms as the NO^2 in the nitro-compound from which it is prepared, but moves one place nearer to the farther bromine-atom, according to a law already explained (p. 189) :



(2.) The modification 1 : 3 : 6 or 1 : 2 : 5, in which the two bromine-atoms are in the para-position with regard to one another, is formed in like manner from nitroparadibromobenzene, $C^6H^2Br^2NO^2$. It melts at 151°-152° (v. Richter).

(3.) The modification 1 : 3 : 4, having the two bromine-atoms in the ortho-position, is formed : a. By passing nitrous acid through a solution of bromamidobenzoic acid, $C^6H^3CO^2H.H.NH^2.Br.H^2$ (p. 270), in glacial acetic acid mixed with excess of hydrobromic acid, and crystallises, after some time, from the solution.

β. By oxidation of dibromotoluene, $C^6H^3.CH^3.H.Br.Br.H^2$ (b. p. 240°), with chromic acid in acetic acid solution.

This acid, purified by separation from its barium salt, crystallises in small colourless needles melting at 227°-230°, sparingly soluble in water, freely in alcohol. The *barium salt*, $(C^6H^3Br^2CO^2)^2Ba + 4\frac{1}{2}H^2O$, is but slightly soluble in pure water, and crystallises therefrom in long colourless needles. The *calcium salt* is deliquescent, and appears to crystallise in small needles. The *copper salt*, $C^6H^3Br^2CO^2.Cu.OH$, separates, on mixing the solution of the barium salt with cupric acetate, as a light blue precipitate insoluble in water. The *silver salt*, $C^6H^3Br^2CO^2Ag$, precipitated from the ammonium salt by silver nitrate, forms a colourless jelly which gradually becomes white and compact. It dissolves in hot water and separates on cooling in dense white masses. The *lead* and *zinc salts* are nearly insoluble in water.

The *ethyl ether*, $C^6H^3Br^2CO^2.C^2H^5$, prepared by decomposing the silver salt with ethyl iodide, crystallises from ether or alcohol in long colourless needles melting at 38°-38.5°.

The *amide*, $C^6H^3Br^2.CO^2NH^2$, is formed by heating the well-dried acid with the requisite quantity of phosphorus pentachloride, and heating the crystalline chloride thereby produced with saturated aqueous ammonia. It crystallises from water in colourless needles melting at 151°-152° (Burghard, *Deut. Chem. Ges. Ber.* viii. 558).

(4.) A fourth dibromobenzoic acid, of unknown constitution, is formed from orthobromobenzoic acid, by nitration, reduction of the nitrobrominated acid with tin and hydrochloric acid, and treatment of the resulting bromamidobenzoic acid with nitrous acid. Its properties have not been described (Burghard).

^c Angerstein's dibromobenzoic acid (m. p. 227°-227°), obtained, together with other products, by direct bromination of benzoic acid, and described in the *2nd Suppl.* (p. 167), as the symmetric modification (1 : 3 : 5), is in all probability identical with the modification here described.

Chlorobenzoic Acids. *Parachlorobenzoic* or *Chlorodracylic acid*, $\text{C}^o\text{H}^4\text{Cl.H.H.COOH}$.—Emmerling (*Deut. Chem. Ges. Ber.* viii. 880) finds that this acid is best prepared by oxidising chlorotoluene with potassium permanganate, which acts much more quickly than nitric acid or a mixture of bichromate and sulphuric acid. One part of commercial chlorotoluene is boiled with 3 pts. of potassium permanganate and a large quantity of water for four to five hours; the remaining permanganate is distilled off; and the hot liquid is filtered and precipitated with sulphuric acid. The product is a mixture of the ortho- and para-acids, in which the former preponderates. They may be separated by boiling water, in which the para-acid dissolves but sparingly. It forms a white earthy mass, subliming in needles and melting at 234° . The silver and sodium salts are anhydrous; the former crystallises well from hot water, and the latter is anhydrous. The *lead salt* is an amorphous precipitate, and the ferric salt resembles ferric benzoate.

The *methyl ether*, $\text{C}^o\text{H}^4\text{ClO}^2\text{CH}^3$, formed by heating the silver salt with methyl iodide, crystallises in beautiful large white needles melting at 42° .

Chlorodracylic acid heated with sodium-amalgam is reduced to benzoic acid (Hartmann, *J. pr. Chem.* [2], xii. 204).

Chlorodracylic chloride, $\text{C}^o\text{H}^4\text{Cl.COCl}$, obtained by heating the acid with phosphorus pentachloride to 140° , is a heavy fuming liquid boiling at 220° – 222° , and having the sp. gr. 1.377. Aqueous ammonia converts it into the *amide*, $\text{C}^o\text{H}^4\text{Cl.CONH}^2$, which is sparingly soluble in cold water, more freely in hot water, and readily in alcohol and ether, crystallising from the latter in needles which melt at 170° . The *anilide*, $\text{C}^o\text{H}^4\text{Cl.CONH}(\text{C}^6\text{H}^5)$, crystallises from alcohol in brilliant needles melting at 194° (Emmerling).

Orthochlorobenzoic or *Chlorosalicylic Chloride*, $\text{C}^o\text{H}^4\text{Cl.COCl}$, obtained by the action of phosphorus pentachloride on orthochlorobenzoic acid, boils at 235° – 236° , and yields with absolute alcohol, an ether which boils at 237° – 241° , and is identical with that which Kekulé obtained from salicylic acid (Emmerling).

Chlorosalicylic acid, fused with caustic potash, yields a mixture of the potassium salts of salicylic and oxybenzoic acids, the latter greatly predominating. With caustic soda, about equal quantities of salicylate and oxybenzoate are obtained. Paroxybenzoate is not formed in either case (Ost, *J. pr. Chem.* [2], xi. 385).

Barium Orthochlorobenzoate separates from hot concentrated solution in anhydrous crystals (Lamprecht a. v. Usler, *Jahresb. f. Chem.* 1857, p. 332; Kekulé, *ibid.* 1860, 293); by spontaneous evaporation crystals are obtained with $3\text{H}^2\text{O}$, 1 mol. of which is given off over sulphuric acid; 100 pts. of water at 18.5° dissolve 31.2 pts. of the anhydrous salt. This salt is but very slightly soluble in hot alcohol, and nearly insoluble in cold alcohol.

The *calcium salt* is also very slightly soluble in hot, quite insoluble in cold alcohol. The *lead salt* is moderately soluble in boiling water, less soluble in alcohol than the β -dichlorobenzoate (Beilstein, *Liebig's Annalen*, clxxix. 283).

Dichlorobenzoic Acids, $\text{C}^o\text{H}^3\text{Cl}^2\text{CO}^2\text{H}$ (Beilstein, *Liebig's Annalen*, clxxix. 283; Aronheim a. Dietrich, *Deut. Chem. Ges. Ber.* viii. 1401; Schultz, *Liebig's Annalen*, clxxxvii. 260). Three of these acids are known, distinguished as α , β , γ . They are all solid at ordinary temperatures, and have the following melting points:—

α	β	γ
201°	156°	122°

α -Dichlorobenzoic acid is produced: 1. By the action of chloride of lime solution on benzoic acid (Beilstein a. Kuhlberg). 2. By oxidising dichlorotoluene with chromic acid (B. a. K.). 3. By heating dichlorobenzene trichloride, $\text{C}^o\text{H}^2\text{Cl}^3\text{CCl}^3$, with water in a sealed tube (Beilstein). 4. By boiling dichlorohippuric acid with strong hydrochloric acid (Otto). 5. By the action of phosphorus pentachloride on sulphochlorobenzoic acid (Otto). See 1st Suppl. p. 312. 6. By the action of potassium chlorate and hydrochloric acid on benzoic acid (Claus, 2nd Suppl. 163). 7. By heating parachlorobenzoic acid to 200° with SbCl^3 (Beilstein a. Kuhlberg, *ibid.*). 8. By oxidising dichlorobenzene chloride, $\text{C}^o\text{H}^2\text{Cl}^2\text{CHCl}^2$, with chromic acid (Beilstein, *Liebig's Annalen*, cl. 294). 9. By the action of alcoholic soda on the crystals formed by treating toluene with excess of chlorine (Pieper, *ibid.* cxlii. 306).

The β -acid (m. p. 156°) is formed: 1. By the action of hydrochloric acid and potassium chlorate on benzoic acid (Claus a. Pfeifer, *Deut. Chem. Ges. Ber.* v. 658; vi. 721). 2. By the action of chloride of lime solution on benzoic acid (Claus a. Thiel, *ibid.* viii. 960). 3. By the action of antimony pentachloride, or of potassium dichromate and hydrochloric acid, on orthochlorobenzoic acid (Beilstein a. Kuhlberg, *ibid.*

viii. 435, 819).^{*} 4. By the action of SbCl_5 on *metachlorobenzoic acid* (Beilstein, *ibid.* iv. 560).

γ Dichlorobenzoic acid is formed, together with the α - and β -acids, by the action of water on dichlorobenzotrichloride:



To prepare the dichlorobenzotrichloride, chlorine gas is passed into dry toluene containing lumps of molybdenum pentachloride, and heated to 70° in a water-bath, and the dichlorotoluene thus formed, after being purified by distillation from molybdenum chloride, is exposed in the state of vapour to the further action of chlorine. The resulting liquid, subjected to fractional distillation, yields between 270° – 280° , a portion having the composition $\text{C}^6\text{H}^3\text{Cl}^3.\text{CCl}_3$ (Schultz).

This dichlorobenzotrichloride is not however a single compound, but a mixture of three isomeric compounds: for when heated with water in sealed tubes, it yields a mixture of three dichlorobenzoic acids, which may be separated through the medium of their barium salts.

For this purpose the mixed acids are boiled with barium hydrate in a capacious flask, with upright condensing tube, till the whole is dissolved; the excess of barium is removed by carbonic acid; the filtered liquid is evaporated to dryness; and the dry residue is boiled for four hours with absolute alcohol, which dissolves the barium dichlorobenzoates, leaving a residue of chloride and carbonate of barium. The alcoholic solution is then freed from alcohol by distillation; the barium salt which remains is dissolved in a large quantity of water; and the filtered solution is left to crystallise. It then deposits fine needles of a barium salt, which, when decomposed by hydrochloric acid, yields a dichlorobenzoic acid, crystallising from water in very slender needles melting at 201° , and agreeing therein, as well as in the composition and properties of its barium salt, $(\text{C}^6\text{H}^3\text{Cl}^3.\text{COO})^2\text{Ba} + 4\text{H}^2\text{O}$, with Beilstein's α -dichlorobenzoic acid (1st Suppl. 312).

The mother-liquor of this α -barium salt yields on further concentration spherical groups of small crystals, from which hydrochloric acid separates an acid melting at 140° – 145° and subliming at 146° ; and further by submitting this barium salt to fractional crystallisation from water, repeated about fifty times, or more quickly by fractional crystallisation from alcohol, it may be separated into two salts, the acids from which melt respectively at 156° and 126.5° .

The acid melting at 156° crystallises from water in slender needles, and sublimes in small but beautiful laminae. Its barium salt, $(\text{C}^6\text{H}^3\text{Cl}^3.\text{COO})^2\text{Ba} + 3\text{H}^2\text{O}$, crystallises from water in warty groups of microscopic needles, from alcohol in small but somewhat more distinct crystals. In these respects the acid in question agrees with the β -dichlorobenzoic acid obtained by Beilstein and by Claus and Pfeifer (2nd Suppl. 183).

The calcium salt of β -dichlorobenzoic acid, $(\text{C}^6\text{H}^3\text{Cl}^3.\text{COO})^2\text{Ca} + 2\text{H}^2\text{O}$, crystallises in needles which do not give off their water in the exsiccator. It is easily soluble in water and in alcohol.

The lead salt, $(\text{C}^6\text{H}^3\text{Cl}^3.\text{COO})^2\text{Pb} + \text{H}^2\text{O}$, obtained by precipitation, is quite insoluble in water, but somewhat soluble in boiling alcohol, from which it is precipitated in needles by water. It does not give off its water of crystallisation over sulphuric acid.

The copper salt, $(\text{C}^6\text{H}^3\text{Cl}^3.\text{COO})^2\text{Cu} + 2\text{H}^2\text{O}$, is a light blue precipitate, insoluble in water and in alcohol.

The ethylic ether, $\text{C}^6\text{H}^3\text{Cl}^3.\text{CO}^2\text{C}^2\text{H}_5$, has a sp. gr. of 1.3278 at 0° , and boils at 271° (thermometer in the vapour).

The amide, $\text{C}^6\text{H}^3\text{Cl}^3.\text{CO}^2\text{NH}_2$, forms shining needles melting at 155° (Beilstein).

The barium salt, when purified by only a few crystallisations, yields an acid melting at 150° , as found by Beilstein (*Liebig's Annalen*, clix. 283); but after a great number of crystallisations, it yields an acid melting at 166° , as found by Claus and Pfeifer.

The γ -acid, which is formed by the process above described in larger quantity than the β -acid, crystallises from alcohol, better than from water, in small needles, melts at 126.5° , volatilises with vapour of water, and sublimes very beautifully even at a lower temperature.

The ammonium salt, $\text{C}^6\text{H}^3\text{Cl}^3.\text{CO}^2\text{NH}_4 + \text{H}^2\text{O}$, formed by decomposing the barium salt with an equivalent quantity of ammonium sulphate, crystallises in needles, and is partially decomposed by boiling with water into ammonia and free acid.

The potassium salt, $\text{C}^6\text{H}^3\text{Cl}^3.\text{CO}^2\text{K} + 5\text{H}^2\text{O}$, prepared in like manner, is very soluble in water, and crystallises therefrom in splendid needles.

The barium salt, $(\text{C}^6\text{H}^3\text{Cl}^3.\text{COO})^2\text{Ba} + 3\frac{1}{2}\text{H}^2\text{O}$, crystallises from alcohol better than from water in stellate groups of small needles. 100 parts of water at 4° dissolve

4.25 g.
salt dissolves in 24 parts of water.

) or 1 pt. of the anhydrous

The *sino salt*, $(\text{O}^{\text{H}}\text{Cl}^{\text{O}}\text{O}^{\text{O}})\text{Zn} + 1\frac{1}{2}\text{H}_2\text{O}$, does not form distinct crystals. It separates from its concentrated solution on boiling, and redissolves on cooling, like calcium citrate. The zinc-salt of the β -acid behaves in the same manner; that of the α -acid does not.

The *cuprio salt* is a blue amorphous powder very slightly soluble in water either hot or cold, also in alcohol. Heated to 200° with water in a sealed tube, it decomposes, with separation of cuprous oxide, and on opening the tube, carbon dioxide escapes, with an odour of phenol.

The chloride, $\text{O}^{\text{H}}\text{Cl}^{\text{O}}\text{CO}^{\text{O}}\text{Cl}$, is a limpid liquid boiling without decomposition at 244° . The amide, $\text{O}^{\text{H}}\text{Cl}^{\text{O}}\text{CO}^{\text{O}}\text{NH}_2$, crystallises from water and from alcohol in white needles melting at 106° .

The following table exhibits a comparative view of the most characteristic properties of the three

Dichlorobenzoic Acids.

Acid	Melting point	Cryst.-water of barium salt	Solubility of barium salt	Zinc salt	Melting point of amide
α	201°	$4\text{H}_2\text{O}$	100 pts. H_2O at 18° dissolve 1.10 parts of the salt (anhydrous).	No separation on boiling.	123°
β	156°	$3\text{H}_2\text{O}$	at 16° , 2.64 pts. of salt.	Separates from concentrated solution on boiling, and redissolves on cooling.	155°
γ	126.5°	$3\frac{1}{2}\text{H}_2\text{O}$	at 4° , 4.7 pts. of salt.		166°

The constitution of the three dichlorobenzoic acids is analogous to that of the dichlorotoluenes from which they are formed. Now the mixture of the three dichlorotoluenes (b. p. 196°), obtained in the manner above described, yields on further chlorination, not a mixture of isomeric compounds, but a single trichlorotoluene, $\text{O}^{\text{H}}\text{Cl}^{\text{O}}\text{CH}_3$, which is crystalline, has a constant melting point (78°), and is converted by strong nitric acid into a single mononitrotrichlorotoluene melting at 88.5° . This shows that the mixture of dichlorotoluenes cannot contain more than three of these isomeric bodies, for a mixture of any four dichlorotoluenes would be convertible by further chlorination into more than one trichlorotoluene. A mixture of three dichlorotoluenes, on the contrary, may yield only a single trichlorotoluene, and in this manner four isomeric trichlorotoluenes may be produced, as shown by the following table in which the group CH_3 is supposed to occupy the position 1.

having its chlorine-atoms in the positions :		Trichlorotoluene may be formed from the three dichlorotoluenes whose chlorine-atoms are in the positions :		
I.	2 :		$2 : 4$	$3 : 4$
II.		$2 : 5$	$2 : 4$	$4 : 5$ (or $3 : 4$)
III.	$2 : 3 : 5$	$2 : 3$	$2 : 5$	$3 : 5$
IV.	$2 : 3 : 6$	$2 : 3$	$2 : 6$	$3 : 6$ (or $2 : 5$)

Two other trichlorotoluenes (making up the six possible modifications) may be formed from the two following pairs of dichlorotoluenes :

V.	$2 : 4 : 6$	—	$2 : 4$	$2 : 6$
VI.	$3 : 4 : 5$	—	$3 : 4$	$3 : 5$

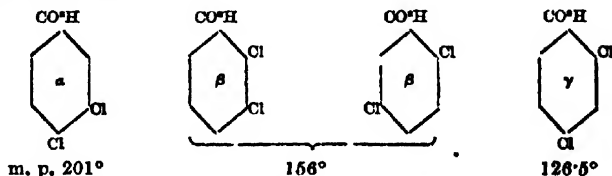
These last may, however, be left out of consideration, as each of them is producible from only two dichlorotoluenes, whereas the mixture of dichlorotoluenes formed by direct chlorination of toluene contains three isomeric modifications. Moreover, two of the first four trichlorotoluenes may also be excluded;

for since all the three dichlorotoluenes in the mixture yield one and the same trichlorotoluene, and since the monochlorotoluene, which is the first product of the chlorination, consists for the most part of the (1 : 4)-compound, it follows that one of the chlorine-atoms in the trichlorotoluene must also be in the position 4. Consequently the trichlorotoluenes III. and IV. may be left out of consideration. There remain, then, only the arrangements I. and II. Now, whichever of these be adopted as representing the constitution of the trichlorotoluene, that of two of the dichlorotoluenes (under B and C) will be the same, viz. 2 : 4 and 3 : 4 (or 4 : 5). The third dichlorotoluene (under A) will, however, have the constitution 2 : 3 or 2 : 5, according as the trichlorotoluene is represented by the formula I. or II.

It remains then to be considered which of the three dichlorobenzoic acids, melting respectively at 201°, 156°, and 126·5°, is analogous in constitution to each of the three dichlorotoluenes 2 : 4, 3 : 4, and 2 : 3 or 2 : 5.

Now α -dichlorobenzoic acid (m. p. 201°) is formed by chlorination of ordinary (1 : 3)-chlorobenzoic acid, and by heating (1 : 4) chlorobenzoic acid with SbCl_5 (p. 262); hence it must have the constitution $\text{CO}_2\text{H} : \text{Cl} : \text{Cl} = 1 : 3 : 4$.

Secondly, β -dichlorobenzoic acid (m. p. 156°) is formed by the action of SbCl_5 on ortho- and on meta-chlorobenzoic acid (p. 262); hence it must have the constitution 1 : 2 : 3, or 1 : 2 : 5; most probably the latter, inasmuch as unsymmetrical modifications appear to be always more readily formed than consecutive modifications. Consequently, there remains for γ -dichlorobenzoic acid (m. p. 126·5°) only the constitution 1 : 2 : 4.*



Iodobenzoic Acid (para- α -), $\text{C}_6\text{H}_4\text{I.H.CO}_2\text{H}$. This acid, which Körner obtained by oxidation of para-iodotoluene, has been further examined by H. Glassner (*Deut. Chem. Ges. Ber.* viii. 562), who has prepared the following salts:—

$\text{C}_6\text{H}_4\text{I.CO}_2\text{Na} + \frac{1}{2}\text{H}_2\text{O}$. Colourless easily soluble needles.

$\text{C}_6\text{H}_4\text{I.CO}_2\text{K}$. Long, thick, apparently rhombic plates, very soluble in water.

$(\text{C}_6\text{H}_4\text{ICO}_2)_2\text{Ca} + \text{H}_2\text{O}$, produced from the sodium salt by decomposition with calcium chloride, forms easily soluble rhombic plates.

$(\text{C}_6\text{H}_4\text{ICO}_2)_2\text{Sr} + \text{H}_2\text{O}$. Colourless nacreous laminæ, crystallising easily from water.

$(\text{C}_6\text{H}_4\text{ICO}_2)_2\text{Ba} + \frac{1}{2}\text{H}_2\text{O}$. Long rhombic plates.

$(\text{C}_6\text{H}_4\text{ICO}_2)_2\text{Zn} + 4\text{H}_2\text{O}$. Cubiform, apparently rhombic crystals, not very soluble.

Paraiodometanitrobenzoic acid, $\text{C}_6\text{H}_3\text{I.NO}_2\text{H.CO}_2\text{H}$, obtained by heating paraiodobenzoic acid with fuming nitric acid, is nearly insoluble in water, easily in alcohol, and melts at 210°. Its *potassium salt*, $\text{C}_6\text{H}_3\text{I}(\text{NO}_2)\text{CO}_2\text{K} + \text{H}_2\text{O}$, forms six-sided prisms truncated by right-angled faces; very soluble in water. The *sodium salt*, also containing 1 mol. water, crystallises in sulphur-yellow easily soluble needles. The *calcium salt*, $[\text{C}_6\text{H}_3\text{I}(\text{NO}_2)\text{CO}_2]_2\text{Ca} + \frac{1}{2}\text{H}_2\text{O}$, forms yellow needles which easily crystallise from water (Glassner).

Nitrobenzoic Acids. The mononitrobenzoic acid, $\text{C}_6\text{H}_5\text{NO}_2\text{CO}_2\text{H}$, obtained by Gerland's process (i. 555)—also recommended by Ernst (*Jahresb.* 1860, 299)—which consists in agitating a mixture of 1 pt. benzoic acid and 2 pts. nitre with 3 pts. strong sulphuric acid (sp. gr. 1·840) is a mixture of the three modifications, ortho-, meta-, and para-, the second being the most and the third the least abundant.

For the separation of the three isomerides the following method is given by Griess (*Deut. Chem. Ges. Ber.* viii. 528). The mixture of the three is heated to boiling with 20 parts of water, and the solution neutralised with baryta; on cooling, barium metanitrobenzoate separates; the filtrate is evaporated almost to dryness, and the residue treated with small quantities of cold water, whereby barium orthonitrobenzoate is readily dissolved, a mixture of the para- and meta-salts being left: this is again boiled

* This last constitution has, however, been generally assigned to the β -acid, on account of its formation by oxidation of dichlorotoluene, which was supposed to be a mixture of only two isomerides, 1 : 3 : 4 and 1 : 2 : 4, derived from panchlorotoluene. But as this dichlorotoluene is now known to be a mixture of three isomerides 1 : 3 : 4, 1 : 2 : 4, and 1 : 2 : 5 (or 1 : 3 : 5), it is just as probable that the β -acid is formed from the third of these dichlorotoluenes as from the second.

with about 20 parts of water, and after cooling the filtrate is acidified with hydrochloric acid, whereby paranitrobenzoic acid is precipitated as a white crystalline mass. After recrystallisation from hot water, this para-acid melts at 233° (Fischer gives 240°, Widmann 238°, and Mills 236°–240°, as the melting point); the barium salt is $[\text{C}^6\text{H}^4(\text{NO}_2)\text{O}]_2\text{Ba} + 5\text{H}_2\text{O}$, as found by Wilbrand and Beilstein in the case of the product from nitrotoluene (1st Suppl. 314). The corresponding *amido-acid* melts at 184° (Wilbrand and Beilstein found 186°–187°).

The amido-acid from *metanitrobenzoic acid* (m. p. 141°) was found by Griess to melt at 172°–174°, as observed also by others.

Orthonitrobenzoic acid may be prepared by oxidising orthonitrocinnamic acid with chromic acid (2nd Suppl. 164); but according to Widmann (*Deut. Chem. Ges. Ber.* viii. 393) this process does not yield satisfactory results. A better method is that of Weith (*ibid.* vii. 1058), which consists in oxidising orthonitrotoluene: the oxidation is slow, but the product is satisfactory. The ortho-acid thus obtained melts at 143°.

Double Salt of Paranitrobenzoic and Benzoic Acids.—When equivalent quantities of these two acids are boiled with water and barium carbonate, and the solution is evaporated, the salt $\left. \begin{matrix} \text{C}^6\text{H}^5\text{CO}_2 \\ \text{C}^6\text{H}^4(\text{NO}_2)\text{CO}_2 \end{matrix} \right\} \text{Ba}$ crystallises out. The same salt is formed by spontaneous evaporation at common temperatures, and this shows that it is not a mixture but a definite compound, inasmuch as both the benzoate and the paranitrobenzoate of barium crystallise at ordinary temperatures in combination with water.

The double salt forms groups of hard, colourless or yellow lenticular crystals. During its formation a few crystals of the paranitrobenzoate occasionally appear: these in one case disappeared, while the crystals of the double salt increased (H. Salkowski, *Deut. Chem. Ges. Ber.* ix. 24).

Other modifications of mononitrobenzoic acid are described by Fittica (*Deut. Chem. Ges. Ber.* viii. 252, 710, 741; ix. 788; x. 481; *Chem. Soc. Jour.* 1875, 766; 1876, ii. 412, 483; further, *Ueber einige besondere Benzolderivate*, Marburg, 1876). (1.) An acid melting at 135°–136°, formed by treating benzoic acid, at a temperature not exceeding 60°, with nitric acid of sp. gr. not higher than 1.42, mixed with an equal quantity of sulphuric acid. By reduction with tin and hydrochloric acid it yields an amido-acid melting at 154°–158°. (2.) An acid melting at 127°, obtained by the action of ethyl nitrate on an ethereal solution of benzoic acid in presence of strong sulphuric acid. Its salts are easily converted by recrystallisation into ordinary metanitrobenzoates, but the free acid is not thus convertible. Its ethylic ether is identical with that of the acid melting at 135° (!). (3.) An acid melting at 128° obtained by dropping a mixture of benzoyl chloride and ethyl nitrate in molecular proportions into strong sulphuric acid at 70°–80°. It crystallises in needles which dissolve in 284.5 parts of water at 16°. (4.) An acid melting at 142°, obtained by dissolving benzoic acid (1 mol.) in strong sulphuric acid, and dropping ethyl nitrate into the solution. It closely resembles the last, but requires for solution 309 parts of water at 16°. (5.) An acid melting at 178°, formed, together with metanitrobenzoic acid and the modification melting at 127°, by adding a mixture of 1 pt. benzoic acid and 2 pts. potassium nitrate to 2 pts. of sulphuric acid. It is contained in the most soluble portion of the mixture of barium salts obtained by neutralising the acid mixture with baryta, and may be further purified by decomposing this barium salt with hydrochloric acid, recrystallising the precipitated nitrobenzoic acids, and dissolving them in milk of lime. On evaporating the solution, the calcium salt of the fifth modification separates out first. The free acid crystallises in yellowish microscopic needles, slightly soluble in cold water, easily in hot water, also in alcohol and ether.

It is, however, very doubtful whether these so-called modifications obtained by Fittica are really definite substances, and the observations of other chemists render it more probable that they are merely mixtures in various proportions of *ortho*-, *meta*-, and *para*-nitrobenzoic acid with one another or with benzoic acid itself. It is known, indeed, that mixtures of organic acids (like certain metallic alloys) do not always melt at temperatures intermediate between the melting points of their components, but sometimes below the melting point of either constituent. Thus according to Leo Liebermann (*Deut. Chem. Ges. Ber.* x. 1038), a mixture of equal parts of:

	m. p.		m. p.
Oxybenzoic acid	200°	and Paraoxybenzoic acid	210°: melts at 143°–152°.
Oxybenzoic acid	200°	and Salicylic acid	155°: „ 120°–134°.
Paraoxybenzoic acid	210°	and Salicylic acid	155°: „ 140°–150°.

Similar results have been obtained with mixtures of stearic acid and some of its lower homologues, viz., palmitic, lauric, and myristic acids (v. 414).

The following observations on the melting points of mixtures of the three mononitrobenzoic acids have been made by E. Widmann (*Deut. Chem. Ges. Ber.* x. 1160):—

M. p.	Ortho 140°	Meta 140°-141°	Para 238°
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A mixture of the three acids in molecular proportions melts at 137°-180°.*

Melting Points of various Mixtures of the Acids C⁶H⁴(NO²).CO²H.

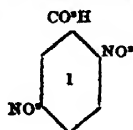
Proportions of the mixture	Ortho and Meta	Ortho and Para	Meta and Para
10 : 10	92°-98°	200°	165°-205°
10 : 5	125°	142°-190°	127°-185°
10 : 1	140°	141°	130°-155°
10 : 0.5	144°	145°	132°-133°
10 : 0.2	146°	147°	134°-135°
10 : 0.1	146°	145°	135°-136°
0.1 : 10	132°-135°	233°-237°	236°-238°
0.2 : 10	132°-134°	228°-235°	232°-237°
0.5 : 10	132°-140°	222°-235°	215°-234°
1 : 10	132°-133°	200°-235°	205°-230°
5 : 10	112°	210°-216°	195°-208°

It is easy to see how mixtures of this kind may exhibit the melting points of Fittica's nitrobenzoic acids.

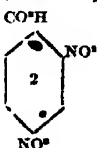
Further, L. Liebermann finds (*loc. cit.*) that when the mixture of *o*-, *m*-, and *p*-nitrobenzoic acid obtained by Gerland's method (p. 265), melting between 115° and 120°, is dissolved in hot water, the solution neutralised, with baryta, and the first portion of the barium salt which crystallises out decomposed by hydrochloric acid, a nitrobenzoic acid is obtained which melts at 122°. On converting this acid into barium salt and proceeding as before, an acid is obtained melting at 125°; and another repetition of this series of processes yields an acid melting at 127°, like one of the nitroacids described by Fittica.

In operating on considerable quantities, Liebermann obtained, by one more crystallisation of the barium salt, two acids, that which separated from the barium salt, which crystallised out first, being pure metanitrobenzoic acid (m. p. 141°-142°), while the acid obtained from the salt which crystallised out gradually as the solution cooled, was found to melt at 135°. On recrystallising this acid from hot water, the portion which separated at once from the hot solution likewise exhibited the characters of pure metanitrobenzoic acid, while the later-crystallising portion separated into two parts, the more soluble exhibiting the characters of orthonitrobenzoic acid, and beginning to melt at 146°-147°, while the less soluble acid melted at 200°, and doubtless consisted of paranitrobenzoic acid mixed with one of the other modifications.

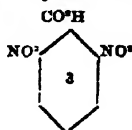
Dinitrobenzoic Acid, C⁶H⁴(NO²)₂.CO²H. Of the six possible modifications of this acid four are known, viz., those represented by the following formulæ:



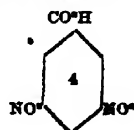
m. p. 140°



m. p. 179°



m. p. 202°



m. p. 204°

One of these has long been known, namely the acid which Cahours obtained by treating benzoic acid with a mixture of nitric and sulphuric acids, and Griess (*Deut. Chem. Ges. Ber.* vii. 1223) has lately obtained three others by similar treatment of ortho-nitrobenzoic acid.

When 1 pt. of orthonitrobenzoic acid is gradually added to a warm mixture of equal parts of fuming nitric and sulphuric acids, and the liquid is then gently boiled

* In this statement and in the table immediately following, where wide intervals of temperature are given, the lowest temperatures denote the commencement of softening, the highest the point at which complete fusion takes place.

for about a quarter of an hour, a product is obtained consisting of three dinitrobenzoic acids, together with styphnic acid; and on pouring the acid liquid into cold water, a large portion of these acids separates at once as a yellowish gradually solidifying oil, the remainder separating only after three or four weeks. The acid mother-liquor is then to be separated by filtration, and the adhering nitric and sulphuric acids removed by washing with water. The four nitro-acids are next converted into barium salts, by boiling the aqueous solution with barium carbonate, and these salts, which differ considerably in solubility, are separated from one another by crystallisation. They are then decomposed by hydrochloric acid, and the acids thereby separated are purified by crystallisation from water.

The three dinitrobenzoic acids thus obtained are represented by the formulæ 1, 2, and 3 above given.

(1.) $\text{CO}^2\text{H} : \text{NO}^2 : \text{NO}^2 = 1 : 2 : 5$. This modification is sparingly soluble in cold, more freely in hot water, and crystallises in needles or large prisms melting at 140° . Its barium salt, $[\text{C}^6\text{H}^2(\text{NO}^2)_2\text{O}^2]^2\text{Ba} + 4\text{H}^2\text{O}$, is sparingly soluble in hot water, and crystallises in white oblong six-sided laminæ. By reduction with tin and hydrochloric acid, this acid is converted into α -diamidobenzoic acid, which by dry distillation yields *paradiamidobenzene*, melting at 140° (*2nd Suppl.* 947). Hence the two NO^2 -groups in this modification of dinitrobenzoic acid must stand to one another in the para-position 1 : 4, and consequently the acid must have the structure 1 : 2 : 5.

(2.) $\text{CO}^2 : \text{NO}^2 : \text{NO}^2 = 1 : 2 : 4$. Another of the three dinitrobenzoic acids obtained as above crystallises from boiling water in long white, highly lustrous, brittle needles, or by slower crystallisation in large rhombic tables or prisms. It is about as soluble in water as the preceding modification, with which it also shares the property of melting under boiling water. It melts in a capillary tube at 179° . When treated with tin and hydrochloric acid it does not yield a diamidobenzoic acid, but is reduced at once to *metadiamidobenzene* melting at 63° . In this respect and likewise in its melting point it agrees with the dinitrobenzoic acid which Tiemann a. Judson obtained by oxidising ordinary dinitrotoluene.

Now this dinitrotoluene is formed by nitration, both of ortho- and of paranitrotoluene (*2nd Suppl.* 924), and must, therefore, have the constitution represented by the formula, $1 : 2 : 4$ or $\text{C}^6\text{H}^4.\text{OH}^2.\text{NO}^2.\text{H}.\text{NO}^2.\text{H}.\text{H}$, and the dinitrobenzoic acid formed from it by oxidation of the group CH^2 to CO^2H , must have a similar constitution, viz., that represented by fig. 2 (p. 237). Its two nitryl-groups are in the meta-position with regard to each other, and, accordingly, it is converted by reduction into meta-diamidobenzene.

The barium salt of this acid is moderately soluble in cold water, and crystallises in white rhombic or hexagonal plates, which in the air-dried state have the composition $[\text{C}^6\text{H}^2(\text{NO}^2)_2\text{O}^2]^2\text{Ba} + 3\text{H}^2\text{O}$, and give off their water of crystallisation at about 180° .

(3.) $\text{CO}^2 : \text{NO}^2 : \text{NO}^2 = 1 : 2 : 6$. The third dinitrobenzoic acid obtained by nitration of orthonitrobenzoic acid, is very soluble in boiling water, and solidifies on cooling from a boiling solution to a pulp of white felted needles melting at 202° . It does not melt under boiling water, like the two acids previously described. Like the other dinitrobenzoic acids, it tastes intensely bitter.

By dry distillation it is resolved into carbon dioxide and metanitrobenzene; and by tin and hydrochloric acid it is at once reduced, like the preceding modification, to metadiamidobenzene. These last two reactions show that the two NO^2 -groups in this acid are in the meta-position with regard to one another, and as one of them occupies the position 2, and the acid is different from the last, the other NO^2 must be at 6, as represented in fig. 3.

The barium salt of this acid is very soluble even in cold water, and crystallises only from a solution evaporated to a syrup. It forms white needles, which in the air-dried state have the composition $[\text{C}^6\text{H}^2(\text{NO}^2)_2\text{O}^2]^2\text{Ba} + 2\text{H}^2\text{O}$, and give off their water at 130° . At higher temperatures the salt decomposes in the same manner as the free acid, yielding carbon dioxide and dinitrobenzene; this decomposition indeed takes place to a slight extent even in the boiling of the aqueous solution.

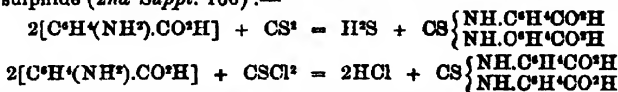
(4.) $\text{CO}^2 : \text{NO}^2 : \text{NO}^2 = 1 : 3 : 5$. This is the ordinary modification, first obtained by treating benzoic acid with a mixture of fuming nitric and sulphuric acids (Cahours. i. 567), afterwards by the action of the same mixture on ordinary (meta-) nitrobenzoic acid (Tiemann a. Judson; Muretow, *2nd Suppl.* 166). It melts at 202° (T. and J.); at 204° - 205° (Muretow). By tin and hydrochloric acid it is reduced to α -diamidobenzoic acid (p. 273), the hydrochloride of which, when distilled with excess of barium hydrate, gives off *metadiamidobenzene* (m. p. 62° - 63°). Consequently its two nitro-groups are in the meta-position relatively to one another; but since it is formed by nitration of metanitrobenzoic acid, one of these groups must be in the

meta-position with regard to the carboxyl; hence this modification is represented by the symmetrical formula, 1 : 3' : 5 (fig. 4).

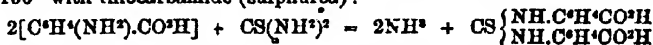
The other two dinitrobenzoic acids in which the two nitril-groups are in the ortho position with regard to each other, viz. 1 : 2 : 3 and 1 : 3 : 4, have not yet been obtained; but the corresponding diamidobenzoic acids are known, viz. those which Griess has designated by the letters β and γ (2nd Suppl. 1187).

On comparing the formulæ of the dinitrobenzoic acids with those of the diamidobenzenes, or phenylenediamines, it will be observed: (1). That paradiamidobenzene can be formed from only one of the dinitrobenzoic acids, viz., 1 : 2 : 5; (2). That orthodiamidobenzene might be formed from two of these acids, viz. 1 : 3 : 4 and 1 : 2 : 3, and has actually been formed from the corresponding diamidobenzoic acids (2nd Suppl. 947,* 1187); and (3), that metadiamidobenzene may be formed from either of the three acids, 1 : 2 : 4, 1 : 2 : 3, and 1 : 3 : 5. All these conclusions are fully confirmed by experiment.

Amidobenzoic Acids, $C^6H^4(NH^2).COOH$. Action of Carbon Sulphochloride on Metamidobenzoic Acid.—When 1 mol. amidobenzoic acid is digested with 2 mols. $CSCl_2$ in a flask with reflux condenser heated in the water-bath, hydrochloric acid and carbon oxy sulphide are abundantly evolved, and the solid mass which remains after twelve hours' digestion, yields to carbon sulphide, as principal product, a substance which, after repeated crystallisation from hot dilute alcohol, exhibits the composition of thiocarbamidobenzoic acid, $CS(NH.C^6H^4.CO^2H)^2$, and is identical with the compound described as *dicarboxylthiocarbamide*, which Merz a. Weith obtained by treating amidobenzoic acid with an alcoholic solution of carbon disulphide (2nd Suppl. 166):—

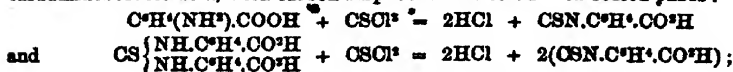


The same compound is obtained, with evolution of ammonia, by heating amidobenzoic acid to 130° with thiocarbamide (sulphurea):

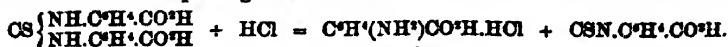


Thiocarbamidobenzoic acid is a white powder which cakes together at 300° , and decomposes at a higher temperature. It is nearly insoluble in water, rather difficult of solution in alcohol, ether, chloroform, and carbon disulphide. It dissolves without decomposition in dilute alkalis, but is decomposed by boiling with strong potash-ley, forming potassium sulphide. When digested with *mercurio oxide*, it exchanges its sulphur for oxygen, and is converted into carbamidobenzoic acid, $CO \begin{Bmatrix} NH.C^6H^4.CO^2H \\ NH.C^6H^4.CO^2H \end{Bmatrix}$, which remains, on evaporation of its aqueous solution, in crystalline crusts, somewhat sparingly soluble in water (Rathke a. Schäfer, *Liebigs Annalen*, clxix. 101).

The portion of the product of the action of carbon sulphochloride on amidobenzoic acid, which is insoluble in carbon sulphide, consists for the most part of the hydrochloride of amidobenzoic acid, which may be dissolved out by water, and there then remains a body insoluble in all the ordinary solvents, and forming a reddish powder when dry. This last compound consists of thiocarbimidobenzoic acid (*Senfölbemzoesäure*), $CS=N.C^6H^4.CO^2H$. It may also be prepared by heating amidobenzoic acid, or thiocarbamidobenzoic acid, with carbon sulphochloride to 140° in sealed tubes:—



also by boiling thiocarbamidobenzoic acid with hydrochloric acid, hydrochloride of amidobenzoic acid then passing into solution:—



Thiocarbimidobenzoic acid is soluble in alkalis and alkaline carbonates, and difficult to purify. Its potash-solution, mixed with a lead salt, deposits lead sulphide when heated. Heated with water and mercuric oxide, it forms mercuric sulphide, and a body easily soluble in water, probably the cyanic acid derivative, $CON.C^6H^4.CO^2H$. Thiocarbimidobenzoic acid unites with *aniline*, forming the compound $CS \begin{Bmatrix} NH.C^6H^4 \\ NH.C^6H^4.CO^2H \end{Bmatrix}$, which melts at 190° – 191° , and is identical with the pro-

* In the article here cited the prefixes *meta*- and *para*- should be reversed.

duct which Merz & Weith obtained (*Deut. Chem. Ges. Ber.* iii. 244), by addition of phenyl-thiocarbimide, $\text{CSN.C}^6\text{H}_5$, to amidobenzoic acid. This body is insoluble in acids, but dissolves in alkalis, alcohol, ether, and hot water, and separates from the solutions on cooling in woolly masses. The sulphur in it is loosely combined, and may be removed by silver nitrate in alcoholic or ammoniacal solution (Rathke & Schäfer).

PARAMIDOBENZOIC OR AMIDODRACYLIC ACID, $\text{C}^6\text{H}_4\text{CO}^2\text{H.H.H.NH}^2\text{H}^2$. According to A. Michael (*Deut. Chem. Ges. Ber.* x. 576), this acid may be advantageously prepared by boiling its oxysuccinyl- or oxyphthalyl-derivative (*infra*) with hydrochloric acid, and decomposing the hydrochloride of amidodracylic acid, which separates on cooling, with sodium carbonate. On acidulating the resulting solution with acetic acid, a precipitate of amidodracylic acid is obtained, melting at 186° – 187° , and exhibiting the other characteristic properties of the acid.

Oxysuccinylparamidobenzoic Acid, $\text{C}^{11}\text{H}^{11}\text{NO}^3 = \text{C}^6\text{H}^4 \begin{smallmatrix} \text{CO}^2\text{NH.C}^6\text{H}^4\text{COOH} \\ \text{CO.OH} \end{smallmatrix}$, is prepared by the action of potassium permanganate in hot aqueous solution on paratolylsuccinimide (obtained by fusing 1 mol. solid toluidine with 1 mol. succinic acid). The quantity of permanganate theoretically required is 2 mols. to 1 mol. tolylsuccinimide, but it is best to use an excess; with 6 mols. permanganate a uniform product is formed, which may be obtained pure by one crystallisation. If, however, the acid is to be used for the preparation of paramidobenzoic acid, a sufficiently pure product may be obtained with 4 mols. of the permanganate.

Oxysuccinylparamidobenzoic acid crystallises in yellowish needles melting at 225° – 226° . (The isomeric acid which Muretow obtained (*2nd Suppl.* 1103) by fusing succinic acid with metamidobenzoic acid melts at 235° .) It is sparingly soluble in cold, somewhat more readily in hot water, moderately soluble in cold, very easily in hot alcohol. It dissolves also very easily in ammonia, and the solution, when concentrated, yields a crystalline *ammonium salt*, very soluble even in cold water. The *barium salt* is obtained, on mixing the concentrated solution of the ammonium salt with barium chloride, as a white precipitate, which dissolves in hot water, and separates therefrom in fine crystalline laminae. The *lead* and *copper salts*, obtained in like manner, are also soluble in hot water; the copper salt is light blue; the *silver salt* is a white flocculent precipitate.

Oxyphthalylparamidobenzoic acid, $\text{C}^{11}\text{H}^{11}\text{NO}^3 = \text{C}^6\text{H}^4 \begin{smallmatrix} \text{CO.NH.C}^6\text{H}^4\text{COOH} \\ \text{COOH} \end{smallmatrix}$, is prepared in like manner by oxidation of paratolylphthalimide, $\text{C}^8\text{H}^{11}\text{NO}^2$, with permanganate (8 mols.); the oxidation proceeds slowly, as the tolylphthalimide is but slightly soluble in hot water. The acid, purified by crystallisation from dilute alcohol, melts at 275° – 277° , and is nearly insoluble in water, whether hot or cold. Its salts resemble those of the preceding acid (Michael).

Bromamidobenzoic Acids, $\text{C}^6\text{H}^3\text{Br}(\text{NH}^2)\text{CO}^2\text{H}$. Two *bromorthamidobenzoic acids*, α and β , have been prepared by Hübner & Petermann (*1st Suppl.* 317). They are obtained by reduction of the corresponding bromonitrobenzoic acids (*ibid.* 315), with tin and hydrochloric acid, care being taken not to continue the action too long or to allow it to become violent, otherwise debromination will take place.

The α -acid, $\text{C}^6\text{H}^3\text{CO}^2\text{H.NH}^2\text{Br.H}^2$, forms colourless needles sparingly soluble in water, melting at 171° – 172° . The *copper salt*, $[\text{C}^6\text{H}^3\text{Br}(\text{NH}^2)\text{CO}^2]_2\text{Cu}$, is pale blue and insoluble in water (Hübner & Petermann). The *silver salt*, $\text{C}^6\text{H}^3\text{Br}(\text{NH}^2).\text{CO}^2\text{Ag}$, prepared from the ammonium salt with silver nitrate, crystallises from water in colourless easily soluble needles. The *lead salt* forms a white precipitate insoluble in water (Hübner & Heinzerling, *Zeitschr. p. Chem.* 1871, 709).

The β -acid crystallises in long colourless needles, very slightly soluble in water, melting at 208° , and volatilising without decomposition.

By the further action of tin and hydrochloric acid, or better by agitating the free acids or their copper salts with sodium-amalgam and a large quantity of water, both these bromamido-acids are converted into orthamidobenzoic (anthranilic) acid (Hübner & Petermann.)

Parabromometamidobenzoic acid, $\text{C}^6\text{H}^3\text{CO}^2\text{H.H.H.NH}^2\text{Br.H}^2$. — Parabromobenzoic acid is converted by nitric acid into metanitroparabromobenzoic acid (m.p. 199°), and this, by the action of tin and hydrochloric acid, into the corresponding bromamido-acid, which crystallises from hot water in colourless and light yellow needles melting at 220° – 221° . It unites both with bases and with acids.

The *hydrochloride*, $\text{C}^6\text{H}^3\text{Br}(\text{NH}^2)\text{CO}^2\text{H.HCl}$, forms colourless needles which turn brown on exposure to light. The *nitrate*, $\text{C}^6\text{H}^3\text{Br}(\text{NH}^2)\text{CO}^2\text{H.NO}^3\text{H}$, forms light

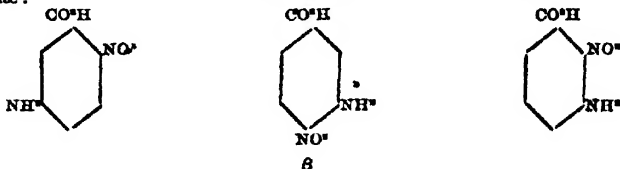
brown flat needles, which are decomposed by water. The *sulphate*, $C^6H^4Br(NH^2)(CO^2H).SO^2H$, forms small needles likewise decomposed by water.

The *copper salt*, $[C^6H^4Br(NH^2)CO^2]^2Cu$, is a bright green precipitate scarcely soluble in water. The *lead salt*, $[C^6H^4Br(NH^2)CO^2]^2Pb$, is a white precipitate insoluble in water (A. Burghard, *Deut. Chem. Ges. Ber.* viii. 558).

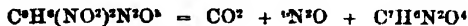
Di-iodometamidobenzoic acids, $C^6H^4I(NH^2).COOH$.—When an alcoholic solution of metamidobenzoic acid, melting at 173° , is treated with iodine and mercuric oxide, mercuric iodide is formed, and the solution acquires a deep red colour. On evaporating the alcohol, extracting the residue with a dilute solution of soda, and adding an acid to the filtered liquid, a violet-coloured precipitate is obtained, consisting of colourless microscopic needles and a red amorphous substance. On boiling this with benzene, the crystals dissolve and separate again on cooling in red needles, which may be purified by treating their alcoholic solution with animal charcoal, and precipitating with water. As, however, the crystalline substance is only slightly soluble in benzene, it is better to dissolve the crude product in alcohol, and to purify it by fractional precipitation with lead acetate, which throws down the red compound first. The substance which crystallises in long colourless needles is di-iodamidobenzoic acid. It is insoluble in water, but easily soluble in alcohol or ether, and in solutions of the caustic and carbonated alkalis. The *potassium salt*, $C^6H^4I(NH^2)CO^2K$, obtained by mixing alcoholic solutions of the acid and of potassium hydrate, crystallises in long silky needles (R. Benedikt, *Deut. Chem. Ges. Ber.* viii. 384).

The red amorphous substance above mentioned is di-iodazobenzoic acid, $C^6H^4I^2NO^2$ (p. 274).

Nitramidobenzoic Acids, $C^6H^4(NO^2)(NH^2).CO^2H$. 1. The three nitramidobenzoic acids derived from uramidobenzoic acid have been already described (2nd Suppl. 1187). As uramidobenzoic acid is a derivative of (1 : 3) amidobenzoic acid, these three nitramido-acids must also have their NH^2 -group in the meta-position with regard to the CO^2H ; and since they are converted by reduction into the three diamidobenzoic acids, α , β , γ (p. 273), their constitution must be represented by the following formulæ:



2. *Nitroparamidobenzoic*, or *Nitramidodracrylic acid*, $C^6H^4NO^2 \rightleftharpoons C^6CO^2H.H.NO^2.NH^2.H^2$, is produced: (1.) By treating uramidodracrylic acid, $C^6H^4NO^2$ (2nd Suppl. 166), with fuming nitric acid, and boiling the resulting dinitrouramidodracrylic acid with water:



(Griess, *Deut. Chem. Ges. Ber.* v. 855).

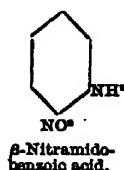
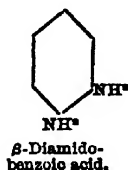
(2.) By the action of aqueous ammonia at high temperatures on nitranisic acid, $C^6CO^2H.H.NO^2.OCH^3.H^2$, the group OCH^3 being replaced by NH^2 . Nitranisic acid or its sodium salt is heated in sealed tubes to 140° . 170° for three or four hours with aqueous ammonia of sp. gr. ≈ 92.0 – 93.0 . When the tubes are charged with free nitranisic acid, a deep brown-red liquid is produced, which, when poured out, solidifies immediately to a mass of red crystalline laminae of ammonium nitramidodracrylate, to be purified by repeated crystallisation from water containing a little ammonia, the salt being somewhat decomposable by pure water. When the tubes have been charged with sodium nitranisate, the resulting solution, after the expulsion of free ammonia by heat, is mixed with hydrochloric acid, the crude nitramidodracrylic acid thereby precipitated is dissolved in ammonia, and the ammonium salt purified as above (H. Salkowski, *Liebigs Annalen*, clixiii. 52).

Nitramidodracrylic acid, separated from the ammonium salt by hydrochloric acid, is a deep yellow precipitate which crystallises from alcohol in tufts of reddish-yellow needles, melting at 284° . It dissolves but slightly in alcohol even at boiling heat, and is insoluble in water (Salkowski); slightly soluble in hot water, more easily in boiling alcohol (Griess). After drying in the air it does not lose weight at 100° .

Potassium Nitramidodracrylate, $C^6H^4(NO^2)(NH^2).CO^2K + H^2O$, prepared by saturating the acid suspended in hot water with the calculated quantity of potassium carbonate, crystallises in orange-coloured prisms. The *silver salt* is a viscid yellow

precipitate. The *barium salt*, $[C^6H^4(NH^2)(NO^2)]^2Ba + 5H^2O$, is but slightly soluble in hot water, and separates on cooling, in orange-coloured needles and laminae.

Nitramidodracrylic acid, though not identical with either of the nitramidobenzoic acids described by Griess, nevertheless gives, when treated with tin and hydrochloric acid, the same diamidobenzoic acid, melting with decomposition at 210° , that is obtained by reduction of β -nitro-amidobenzoic acid from β -dinitro-uramidobenzoic acid (2nd Suppl. 1187): hence it has the constitution represented by the first of the following figures:—

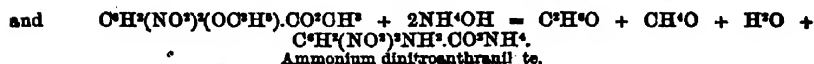


Nitro-amidodracrylic acid, boiled with potash-ley, is converted, by exchange of NH^2 for OH , into oxynitrodacrylic acid, $C^4.CO^2H.H.NO^2.OH.H^2$, and β -nitro-amidobenzoic acid, in like manner into the isomeric compound, β -oxynitrobenzoic acid, $C^6.CO^2H.H.OH.NO^2.H^2$ (Griess,).

Nitro-amidodracrylic acid, treated with a cold solution of nitrous acid in absolute alcohol, is converted into nitroparadiazobenzoic acid, $(C^6H^4(NO^2)^2N^2O^2)$, which, when boiled with alcohol, yields ordinary (meta-) nitrobenzoic acid. If, on the other hand, the nitroamidodracrylic acid be treated with a warm alcoholic solution of nitrous acid, a semi-fluid mass is formed, partly soluble in ammonia, the insoluble portion apparently consisting of ethylic nitrobenzoate, while the ammoniacal solution mixed with hydrochloric acid yields a precipitate which, when purified by recrystallisation and finally by distillation with water, melts at 150° , and has the composition of chlorobenzoic acid, $C^6H^4ClO^2$ (Salkowski).

Nitro-orthamidobenzoic acids.—Of this acid there are two known modifications (α -1:2:6 and β -1:2:3). They are formed by heating the diethylic ethers of the corresponding nitrosalicylic acids, $C^6H^4(NO^2)(OH).CO^2H$, with alcoholic ammonia, and decomposing the resulting nitramidobenzamides, $C^6H^4(NO^2)(NH^2).CO^2(NH^2)$, by boiling with baryta-water. Both acids crystallise in long needles. The α -acid melts at 270° ; the β -acid at 205° . Both are reduced by sodium-amalgam to ortho-amidobenzoic (anthranilic) acid.

3. *Dinitro-orthamidobenzoic or Dinitro-anthranilic acid*, $C^6H^4(NO^2)^2NH^2.CO^2H$ (H. Salkowski, *Liebig's Annalen*, clxxiii. 40).—This acid is formed, together with its methylic ether, by heating the methylic ether of dinitroethylsalicylic acid with excess of aqueous ammonia on the water-bath:

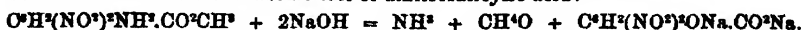


The solid product of the reaction is pulverised, again treated with ammonia, then washed, dried, and crystallised from hot alcohol, whereby crystalline laminae are obtained, consisting of the methylic ether of dinitroanthranilic acid. The ammoniacal solution, when freed from excess of ammonia, gives with hydrochloric acid a deep yellow precipitate of dinitroanthranilic acid, small in quantity in comparison with the solid product of the reaction. The acid is washed, dried, crystallised from boiling alcohol, and redissolved in ammonia; the ammoniacal solution is evaporated to the crystallising point; and these operations are repeated several times in order to remove a small quantity of the still remaining methylic ether. In this manner two kinds of crystals are obtained, one darker-coloured, the other lighter (like the α - and β -chrysanisate), but nevertheless identical in composition.

Dinitroanthranilic acid, separated from the purified ammonium salt by hydrochloric acid, is a deep yellow precipitate, and crystallises from alcohol, in which it is slightly soluble, in golden-yellow scales, very much like chrysanisic acid. It melts at 255° (chrysanisic acid at 258°).

The ammonium salt, $C^6H^4(NO^2)_2NH^2.CO^2NH^4 + H^2O$, forms yellow or brown needles.

The methyl ether crystallises from hot alcohol in narrow yellow laminae or feathery groups of needles, melting at 165° . It is slightly soluble in boiling alcohol, very slightly in cold alcohol, insoluble in water. It is scarcely attacked by a boiling solution of sodium carbonate, but when boiled with caustic soda, it gives off ammonia, and is converted into the disodic salt of dinitrosalieylic acid:



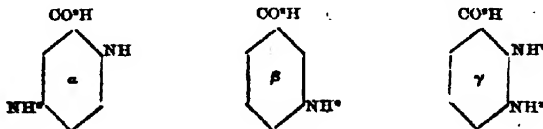
The ethylic ether, $C^6H^4(NO^2)_2NH^2.CO^2C^2H^5$, prepared by passing hydrochloric acid gas into the alcoholic solution of the acid, precipitating with water, washing with dilute ammonia, and recrystallising from hot alcohol, forms yellow laminae melting at 135° , and only sparingly soluble in alcohol even at the boiling heat.

On Dinitroparamidobenzoic or Chrysanisic acid, see 2nd Suppl. 336.

Diamidobenzoic Acid, $C^6H^4(NH^2)_2.COOH$. (Griess, *Liebig's Annalen*, cliv. 325; *J. pr. Chem.* [2], vi. 927; *Deut. Chem. Ges. Ber.* v. 192, vii. 1223; *Proc. Roy. Soc.* xx. 168; Wurster a. Ambühl, *Deut. Chem. Ges. Ber.* vii. 213; Meyer a. Wurster, *ibid.* v. 635; *Liebig's Annalen*, clxxi. 62; H. Salkowski, *ibid.* clxxiii. 56, 66). Griess, by boiling the three dinitro-uramidobenzoic acids, $C^6H^4(NO^2)_2N^2O^2$ (2nd Suppl. 1186) with water, obtained the three corresponding nitroamidobenzoic acids, $C^6H^4(NO^2)(NH^2).COOH$; and these by reduction with tin and hydrochloric acid yield the three corresponding diamidobenzoic acids (distinguished as α , β , and γ). These latter are resolved by dry distillation into carbon dioxide and diamidobenzenes or phenylene-diamines, $C^6H^4(NH^2)_2$, the α -acid yielding paradiamidobenzene, and the other two yielding orthodiamidobenzene, whence it follows that the α -diamidobenzoic acid has the two NH^2 -groups in the position 1 : 4, while in the β - and γ -acids they are in the position 1 : 2. Further, Salkowski has shown that Griess's β -diamidobenzoic acid is identical with that which is obtained by heating nitranisic (nitromethylpara-oxybenzoic) acid with aqueous ammonia, to 140° – 170° in sealed tubes, whereby it is converted into nitroparamidobenzoic acid, and reducing the latter with tin and hydrochloric acid. Now, remembering that this diamidobenzoic acid is resolved by distillation into CO^2 and orthodiamidobenzene, it is evident that the nitroparamidobenzoic acid from which it is formed must have the NO^2 - and NH^2 -groups in the ortho-position. Consequently, nitranisic acid and nitroparamidobenzoic acid must be represented by the following formulae:



and the three diamidobenzoic acids obtained by Griess, as above mentioned, by the formulae:



The three metadiamidobenzoic acids, 1 : 2 : 4, 1 : 2 : 6, and 1 : 3 : 5 (CO^2H in 1), are formed by reduction of the corresponding dinitrobenzoic acids (p. 267), and are resolved by distillation into CO^2 and metadiamidobenzene.

The symmetrical modification (1 : 3 : 5) was discovered by Voit in 1856 (iv. 294), and has been further examined by Griess (*Liebig's Annalen*, [1870], cliv. 325), who finds that it crystallises from water in long nearly white needles melting at about 240° when quickly heated, but not sublimable without decomposition; 1000 pts. of water dissolve 11 pts. of the acid; alcohol and ether dissolve it more readily. It unites (contrary to Voit's statement) with bases as well as with acids. The barium salt, $[C^6H^3(NH^2)_3O^2]^2Ba + 1\frac{1}{2}H^2O$, crystallises in whitish to honey-yellow prisms or spiculae, easily soluble in water, less easily in alcohol. The silver salt, $C^6H^3(NH^2)_3O^2Ag + 2H^2O$, forms white microscopic needles; the lead salt narrow laminae. The hydrochloride crystallises in white easily soluble needles; the nitrate in long laminae, easily soluble in hot water, less easily in cold water and in alcohol; the oxalate in small slightly soluble rhombic prisms.

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The acid, treated with excess of *bromine water*, is converted into tribromodiamidobenzoic acid, $\text{C}^6\text{Br}^3(\text{NH}^2)^2\text{CO}^2\text{H}$.

Base obtained by the action of Methyl iodide on 1:3:5 Diamidobenzoic acid.—When 1 pt. of this acid is mixed with 10 pts. of methyl alcohol and twice as much concentrated potash as is required for neutralising the acid, and 6 mols. of methyl iodide are then added for each molecule of diamidobenzoic acid present, a brisk reaction sets in, and the liquid soon becomes acid. On adding more potash, and repeating this treatment till the liquid remains alkaline even after the addition of more methyl iodide, a product is obtained, containing the elements of 2 mols. hydriodic acid and 1 mol. hexmethyldiamidobenzoic acid, $\text{C}^6\text{H}^2(\text{CH}^3)^4\text{N}^2\text{O}^2\cdot 2\text{HI} + \text{H}^2\text{O}$, but really consisting of the di-iodide of an ammonium base, $[\text{C}^6\text{H}^4(\text{CH}^3)^4\text{O}^2]\text{N}^2\cdot\text{I}^2 + \text{H}^2\text{O}$. The aqueous solution of this iodide, mixed with a solution of iodine in potassium iodide, yields a periodide which separates in slender brownish-yellow needles.

This so-called free acid—more probably base or hydroxide— $[\text{C}^6\text{H}^4(\text{CH}^3)^4\text{O}^2]\text{N}^2\cdot(\text{OH})^2$, is obtained by decomposing the hydriodic acid with moist silver oxide. It forms a very hygroscopic crystalline mass, consisting of soft white plates, and is as caustic and alkaline as potash. Its aqueous solution destroys the epidermis, precipitates metallic salts, and rapidly absorbs carbon dioxide. The *chloride*, $[\text{C}^6\text{H}^4(\text{CH}^3)^4\text{O}^2]\text{N}^2\cdot\text{Cl}^2 + 4\text{H}^2\text{O}$, may be obtained by neutralising the base with hydrochloric acid, or more conveniently, by decomposing the iodide with silver chloride. It is very soluble in water, sparingly in hot, and still less soluble in cold alcohol, and forms small, white, glistening six-sided plates, which lose their water at 100° . The *platinochloride*, $[\text{C}^6\text{H}^4(\text{CH}^3)^4\text{O}^2]\text{N}^2\cdot\text{Cl}^2\cdot\text{PtCl}^4 + \text{H}^2\text{O}$, is a precipitate consisting of very small, pale-yellow plates, commonly grouped in stars. The *carbonate*, $[\text{C}^6\text{H}^4(\text{CH}^3)^4\text{O}^2]\text{N}^2\cdot\text{CO}^2 + 3\text{H}^2\text{O}$, is formed by decomposing the iodide with silver carbonate, and crystallises from water in small, very soluble plates having an alkaline reaction (Griess, *Deut. Chem. Ges. Ber.* vii. 39).

Triamidobenzoic Acid, $\text{C}^6\cdot\text{CO}^2\text{H}\cdot\text{NH}^2\cdot\text{H}\cdot\text{NH}^2\cdot\text{NH}^2\cdot\text{H}$. Produced by reduction of dinitroparamidobenzoic (chrysanisic) acid (2nd Suppl. 167).

Azobenzoic Acid, $\text{C}^6\text{H}^5\text{N}^2\text{O}^4$. According to Fittica (*Deut. Chem. Ges. Ber.* vii. 252), the ethylic ether of ordinary azobenzoic acid melts at 97° , that of parazobenzoic or azodraeylic acid at 88° .

Action of Ethyl Iodide on Silver Azobenzoate.—This reaction yields two compounds: (1) A bibasic acid, $\text{C}^6\text{H}^4(\text{C}^2\text{H}^5)^2\text{N}^2\text{O}^4$, crystallising in nearly white needles, and forming well-crystallised salts, the silver salt having the composition $\text{C}^6\text{H}^4\text{Ag}^2(\text{C}^2\text{H}^5)^2\text{N}^2\text{O}^4$, the barium salt $\text{C}^6\text{H}^4\text{Ba}(\text{C}^2\text{H}^5)^2\text{N}^2\text{O}^4$.

(2) A body which forms irregular crystals melting at $74^\circ\text{--}76^\circ$, different therefore from Strecker's ethyl azobenzoate (1st Suppl. 321), which melts at $90^\circ\text{--}92^\circ$. Both these compounds when treated with alcoholic potash yield an acid having the composition $\text{C}^6\text{H}^4\text{N}^2\text{O}^4$ or $\text{C}^6\text{H}^2(\text{C}^2\text{H}^5)^2\text{N}^2\text{O}^4$ (Golubeff, *Deut. Chem. Ges. Ber.* vii. 1651).

Di-iodazobenzoic acid, $\text{C}^6\text{H}^2\text{I}^2\text{N}^2\text{O}^4 \rightleftharpoons \text{C}^6\text{H}^2\text{I} \begin{array}{c} \text{N} \\ \text{COOH} \end{array} \begin{array}{c} \text{N} \\ \text{COOH} \end{array} \text{C}^6\text{H}^2\text{I}$, is the red substance formed, together with di-iodamidobenzoic acid, by the action of iodine and mercuric oxide on metamidobenzoic acid (p. 271). It may be separated from the amido-acid by fractional precipitation with lead acetate, and obtained in the free state by decomposing its lead salt with hydrogen sulphide. Like most azo-acids it is amorphous and easily soluble in acids and alkalis. Its alkaline solution treated with sodium-amalgam rapidly becomes yellow, but again acquires a brownish-red tint on exposure to the air (Benedict, *Deut. Chem. Ges. Ber.* viii. 384).

Dinitrazobenzoic acid, $\text{C}^6\text{H}^4(\text{NO}^2)^2\text{N}^2\text{O}^4$.—This acid is obtained by boiling freshly precipitated azobenzoic acid (from ordinary nitrobenzoic acid) with nitric acid of sp. gr. 1.52. It is crystallisable, insoluble in cold water, and sparingly soluble in hot water and in alcohol. It does not melt when heated, but is decomposed with detonation. Its salts also detonate. The salts of the alkali-metals are easily soluble in water, insoluble in alcohol, and crystalline. The *barium*, *cadmium*, and *calcium* salts are obtained as crystalline precipitates. The *ethylic ether*, $\text{C}^6\text{H}^4(\text{C}^2\text{H}^5)^2(\text{NO}^2)^2\text{N}^2\text{O}^4$, is a solid crystalline substance (Golubeff, *ibid.* 487).

Diazobenzoic Compounds (Griess, *Deut. Chem. Ges. Ber.* ix. 1653). Orthodiazobenzoic nitrate, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2\cdot\text{NHO}^3$ or $\text{C}^6\text{H}^4\text{N}^2\text{O}^2\cdot\text{NO}^3$, is prepared by passing nitrous acid vapour into an ice-cooled pasty mixture of orthamidobenzoic (anthranilic) nitrate and nitric acid previously diluted with an equal volume of water, till the whole is dissolved and an excess of nitrous acid is present, which may be easily recognised by the odour. On mixing the resulting solution with strong alcohol, and adding ether, the nitrate separates in white rhombic six-sided tables or prisms. It dissolves

very easily in cold water, somewhat less in alcohol, and explodes violently when heated. On boiling its aqueous solution, the compound is resolved into salicylic acid, nitric acid, and free nitrogen:



A basic nitrate, $2\text{C}^6\text{H}^4\text{N}^2\text{O}^2.\text{NO}^2\text{H}$, is produced by dissolving the preceding compound in a small quantity of cold water, adding alcohol and ether, and repeating these operations several times on the crystals which separate out. It is thus obtained in long white needles, which agree in almost all their characters with the normal nitrate, especially in their reaction with boiling water:

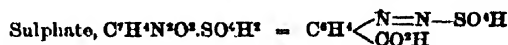
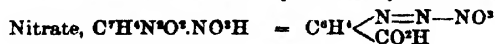


Metadiazobenzoic Sulphate, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2.\text{SO}^4\text{H}^2$, is prepared, like the preceding compound, by passing nitrous acid in excess into a thin paste of amidobenzoic sulphate and dilute sulphuric acid, and separates immediately in the crystalline form, on filtering the solution from the very sparingly soluble metadiazobenzoic nitrate which forms at the same time, and mixing the filtrate with alcohol and ether. It forms nearly white, long, narrow laminae, extremely soluble in water, and decomposing with detonation when heated.

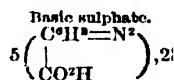
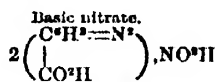
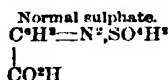
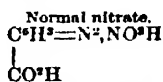
A basic sulphate, $5\text{C}^6\text{H}^4\text{N}^2\text{O}^2.2\text{SO}^4\text{H}^2$, is prepared from the preceding salt in the same manner as the basic nitrate from the normal nitrate, and crystallises in small needles, which decompose when their aqueous solution is boiled, yielding oxybenzoic acid, sulphuric acid and free nitrogen:



According to Kekulé's view of the constitution of the diazo-compounds (1st Suppl. 209), the normal salts above described are represented by the following formulæ:



Griess objects to this view, on the ground that it does not explain the constitution of the basic salts just described. and he represents these and the normal salts by the following formulæ:



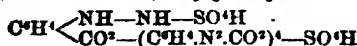
These formulæ, however, give no insight into the constitution of the salts, but merely express that the molecules $\text{C}^6\text{H}^4\text{N}^2\text{O}^2$ and NO^2H or SO^4H^2 are united in certain proportions in a manner which cannot at present be explained.

If, on the other hand, we adopt Kekulé's view, the basic nitrate, $\text{C}^6\text{H}^4\text{N}^4\text{O}^2$, may be represented by the constitutional formula:

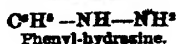


and the same mode of representation might obviously be extended to atri-basic, quadri-basic nitrate, &c.

The $\frac{5}{2}$ -basic sulphate, $\text{C}^6\text{H}^4\text{N}^4\text{S}^2\text{O}^{12}$, may perhaps be formulated as follows:

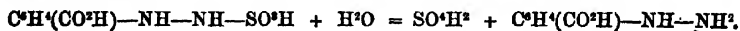


Hydrodiazobenzoic acid, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2 = \text{C}^6\text{H}^4 \begin{array}{l} \text{NH}-\text{NH}^2 \\ | \\ \text{CO}^2\text{H} \end{array}$.—This acid is related to the metadiazobenzoic compounds in the same manner as phenyl-hydrazine (q.v.) to the diazobenzene compounds:

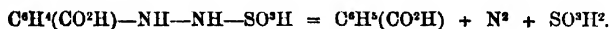


To prepare it, metadiazobenzoic nitrate (1 pt.) triturated with water is gradually added to a cold concentrated solution of neutral potassium sulphite (2 pts.), and the liquid is gently warmed, and mixed with excess of hydrochloric acid; it then, on cooling, yields an abundant crystallisation of potassium diazosulphobenzoate, $C^6H^4(CO^2H).N^2.SO^2K$, in light yellow, long, narrow laminae, which detonate strongly when heated. On treating this salt with tin and hydrochloric acid, removing the tin from the resulting solution with hydrogen sulphide, and evaporating the filtrate till it begins to crystallise, then supersaturating with ammonia, and finally adding excess of acetic acid, hydrodiazobenzoic acid separates on cooling in brownish crystals, which may easily be obtained quite pure by recrystallisation from boiling water, with addition of animal charcoal.

Hydrodiazobenzoic acid may also be prepared (similarly to phenyl-hydrazine) by treating potassium diazosulphobenzoate with zinc and acetic acid, whereby it is converted, by assumption of H^2 , into the hydrodiazosulphobenzoate, $C^6H^4(CO^2H)-NH-NH-SO^2K$, which may be obtained by precipitating the zinc with hydrogen sulphide, filtering and evaporating, in small nodules easily soluble in hot water,—and boiling this salt with hydrochloric acid, whereby the hydrodiazosulphobenzoic acid is resolved, with assumption of water, into sulphuric and hydrodiazobenzoic acids :



If, on the other hand, the hydrodiazosulphobenzoate be boiled with strong potash-ley, its nitrogen is given off as gas, and the product consists of benzoic and sulphurous acids ; thus :



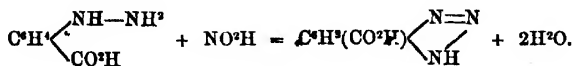
Hydrodiazobenzoic acid crystallises in faintly yellowish laminae, which, according to circumstances, are either elliptical or 3 to 6-sided. It is tasteless and inodorous ; in a capillary tube it melts with frothing and decomposition, at 186° . It is but slightly soluble in hot, still less in cold water or alcohol ; quite insoluble in ether ; exhibits a strong acid reaction with vegetable colours.

Hydrodiazobenzoic acid unites with hydrochloric acid, forming the compound $C^6H^4N^2O^2.HCl$, which dissolves easily in hot, somewhat sparingly in cold water, and separates from the solution on addition of hydrochloric acid, in white needles or long narrow laminae.

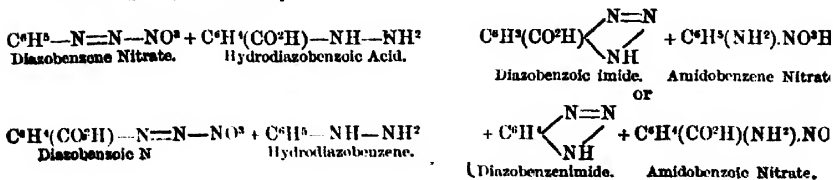
Barium Hydrodiazobenzoate, $(C^6H^4N^2O^2)Ba + 4H^2O$, obtained by dissolving barium carbonate in the hot aqueous acid, crystallises in small nodules very soluble in water.

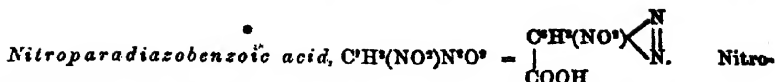
Hydrodiazobenzoic acid closely resembles phenyl-hydrazine in nearly all its reactions, especially in its easy reducibility by certain metallic salts and by Fehling's solution. With nitrous acid, however, it behaves somewhat differently ; for whereas phenyl-hydrazine is thereby converted into phenyl-nitrosylhydrazine, $C^6H^5N^2(NO)$,

which easily splits up into water and diazobenzenimide, $C^6H^4 \begin{smallmatrix} N=N \\ \diagup \quad \diagdown \\ NH \end{smallmatrix}$, hydrodiazobenzoic acid on the other hand, is directly converted into the imide of diazobenzoic acid ; thus :

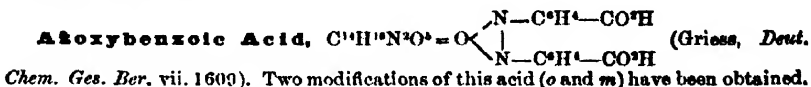


Diazobenzoic imide is also formed, together with diazobenzenimide, aniline and amidobenzoic acid, by the action of diazobenzene nitrate on hydrodiazobenzoic acid, and the same bodies are formed by the action of diazobenzoic nitrate on hydrodiazobenzene (phenyl-hydrazine).





paramidobenzoic acid added to cold absolute alcohol nearly saturated with nitrous acid, is converted, sometimes immediately, sometimes in the course of a day, into small light yellow laminae of nitroparadiazobenzoic acid, which may be washed with alcohol, and dried, first in the air, afterwards over sulphuric acid. This acid explodes violently when struck or heated, but may be burnt when mixed with a large excess of copper oxide. It is nearly insoluble in cold alcohol, and is easily decomposed by boiling alcohol, being converted into metanitrobenzoic acid (Salkowski, *Liebig's Annalen*, clxxiii. 63).



Two modifications of this acid (*o* and *m*) have been obtained. *Ortho-azoxybenzoic acid*, ($\text{CO}^2\text{H} : \text{N} = 1 : 2$), formed by reduction of ortho-nitrobenzoic (nitrosalylic) acid with sodium-amalgam, crystallises in white rhombic prisms, moderately soluble in hot, somewhat sparingly in cold alcohol, still less in ether and in boiling water. When heated, it melts, blackens, and decomposes. The barium salt, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2\text{Ba} + \text{H}^2\text{O}$, crystallises in white spicular crystals, easily soluble even in cold water. By treatment with sodium-amalgam, this acid is converted, first into orthazobenzoic and then into orthohydrazobenzoic acid, the latter of which is separated from the resulting solution by acetic acid as a white precipitate, and crystallises from boiling alcohol in small elongated leaflets or microscopic prisms. It is permanent when dry, but in the moist state (and more quickly when treated with nitrous acid), it is reconverted into orthazobenzoic acid. It unites with bases but not with acids, acquiring the latter property, however, when boiled with hydrochloric acid, and yielding a hydrochloride, which forms with platinum chloride a highly characteristic double salt, crystallising in insoluble light-yellow needles. On treating the solution of the hydrochloride with ammonia and acetic acid, a new acid separates in slender siskin-green needles, slightly soluble in boiling alcohol and ether: it has not been analysed, but probably consists of *orthodiamidodiphenic acid*.

Meta-azoxybenzoic acid, ($\text{CO}^2\text{H} : \text{N} = 1 : 3$), was first obtained by Griess in 1864, by boiling an alcoholic solution of metanitrobenzoic acid with solid potassium hydrate (1st *Suppl.* 322). When boiled for some hours with tin and hydrochloric acid, it is partly reduced to common amidobenzoic acid, and partly to an amido-acid, which crystallises in short white needles, having the composition $\text{C}^6\text{H}^4\text{N}^2\text{O}^2 + 1\frac{1}{2}\text{H}^2\text{O}$. They lose their water at 150° , and are sparingly soluble in boiling water and alcohol, and almost insoluble in ether. On heating the residue to 170° , it melts and undergoes a molecular change, being converted into an amorphous mass, which is almost insoluble in all neutral solvents, but still possesses the character of an amido-acid.

The silver salt of this amido-acid, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2\text{Ag}^2 + \text{H}^2\text{O}$, is an amorphous precipitate, which is formed by adding silver nitrate to an ammoniacal solution of the acid; on standing it soon changes into small plates, grouped in stars.

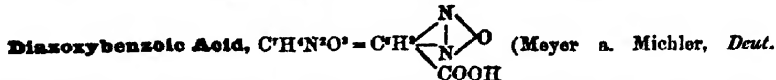
The hydrochloride, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2 \cdot 2\text{HCl}$, crystallises in white prisms, which are freely soluble in hot water, sparingly in cold water, less soluble in hydrochloric acid.

The platinumchloride, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2 \cdot 2\text{HCl} + \text{PtCl}_4 + 2\text{H}^2\text{O}$, forms either small, mammellated crystals, or well-defined rhombic prisms, or plates; it is sparingly soluble in cold water, and slowly decomposed on boiling the solution.

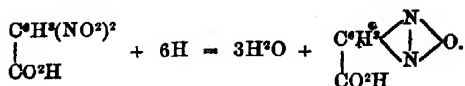
When the barium salt of this amido-acid is distilled with baryta, it is resolved into carbon dioxide and benzidine (diamido-diphenyl):



The acid is therefore diamidodiphenic acid, $\text{C}^6\text{H}^4(\text{NH}_2)_2 \begin{array}{c} \diagup \text{COOH} \\ \diagdown \text{COOH} \end{array}$, and stands to Strecker's hydrazobenzoic acid, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2$ (1st *Suppl.* 321), in the same relation as benzidine to hydrazobenzene. Hydrazobenzoic acid does not combine with hydrochloric acid, but when boiled therewith is converted into diamidodiphenic acid.



—This acid is formed by the action of nascent hydrogen on dinitrobenzoic acid:



When 8 molecular weights of 5 per cent. sodium-amalgam are gradually added to a solution of 1 molecular weight of ordinary dinitrobenzoic acid (m. p. 204°), a clear but perfectly black liquid is obtained (or brown if very dilute), from which hydrochloric acid throws down the diazo-acid in black flocks, while the aqueous solution becomes colourless. Neither the acid nor its alkaline solution loses its dark colour when treated with animal charcoal, the colour being in fact a characteristic property of the acid. The pure acid when dry is an amorphous shining black powder resembling animal charcoal, and decomposing with decrepitation when heated. It is insoluble in alcohol, ether, benzene, chloroform, and glacial acetic acid. In potash, soda, and ammonia it dissolves easily and completely, forming deep brown solutions from which it is precipitated unchanged by acids.

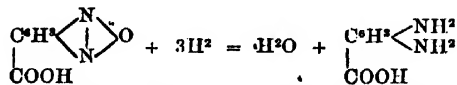
The ammonium salt dries up on evaporation to a brown transparent varnish.

The silver salt, $\text{C}^6\text{H}^4\text{N}^2\text{O} \cdot \text{CO}^2\text{Ag}$, is a black bulky precipitate, easily soluble in strong aqueous ammonia, and forming, when dry, an amorphous powder, which decomposes with strong decrepitation when heated.

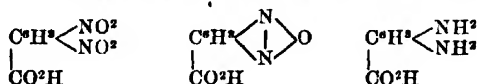
The barium salt, $(\text{C}^6\text{H}^4\text{N}^2\text{O} \cdot \text{COO})^2\text{Ba}$, is a very bulky black precipitate, shrinking up to a small mass when dried, and yielding a black powder which decrepitates when heated, leaving a bulky carbonaceous residuo. When dried at 70°-120° it becomes so highly electric that its particles jump about in the basin for hours.

The zinc salt, $(\text{C}^6\text{H}^4\text{N}^2\text{O} \cdot \text{COO})^2\text{Zn}$, is a brownish-black amorphous precipitate, insoluble in water, and drying up to an amorphous powder which decrepitates less strongly than the silver or barium salt.

Diazoxybenzoic acid is reduced by tin and hydrochloric acid to diamidobenzoic acid:



It is intermediate in composition between dinitrobenzoic and diamidobenzoic acids:



It appears, moreover, to be related to the humus and ulmin class of compounds. Bodies of this character have, in fact, been obtained by Hofmann a. Geyzer (*Jahrb. f. Chem.* 1872, 771), by the action of sodium on chloronitrobenzenes, and Emmerling a. Jacobsen (*ibid.* 1871, 741) regard some of the ulmin-substances which they have examined as azo-compounds.

Mononitrodiazoxybenzoic acid, prepared by digesting diazoxybenzoic acid with fuming nitric acid at 100°, forms amorphous red-brown flocks resembling ferric hydrate insoluble in all the ordinary solvents, dissolving with deep, brown colour in alkalis; its metallic salts form black amorphous precipitates. It is remarkable that this acid is not reduced by boiling with tin and hydrochloric acid (Michler).

Isodiazoxybenzoic acid.—This isomeride of the acid just described is formed by the action of sodium-amalgam on dinitrobenzoic acid (4 : 2 : 4), melting at 179°. It exactly resembles the preceding acid in all its external characters, but differs essentially therefrom in its behaviour to tin and hydrochloric acid, by which indeed it is not attacked even after prolonged boiling (Michler).

Oxybenzoic Acids, $\text{C}^6\text{H}^4 \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{COOH} \end{array}$

(i). **Ortho-oxybenzoic or Salicylic Acid, $\text{C}^6\text{H}^4\text{CO}^2\text{H} \cdot \text{OH} \cdot \text{H}^4$.** On the preparation of this acid by the action of carbon dioxide on sodium-phenol, see 2nd Suppl. 1065.

largely of salicylic acid; at still higher temperatures the amount of salicylic acid produced is much less.

On the converse reaction, i.e. conversion of salicylic into paraoxybenzoic acid, see p. 286.

Purification.—Crude salicylic acid may be purified by heating it to 170° with steam in a copper vessel with double walls, the space between them being filled with paraffin heated to 170° . The snow-white acid thereby obtained still retains traces of phenol, from which it may be freed by recrystallisation from water. Salicylic acid is scarcely volatilised by over-heated steam (*A. Rauter, Dent. Chem. Ges. Ber.* viii, 537).

According to J. C. Thresh (*Pharm. J. Trans.* [3], vi, 43) the colour of commercial salicylic acid may be removed by dissolving it, with aid of heat, in four times its weight of glycerin, and reprecipitating with excess of cold water; but, according to a statement in the *Pharmaceutische Zeitung*, the solution of 1 part salicylic acid in 50 parts glycerin remains clear on cooling, and does not yield any precipitate on dilution with water.

For testing the purity of salicylic acid, the following process is given by Kalbe (*J. pr. Chem.* [2], xiv, 143). Half a gram of the acid is dissolved in about five grams of strong alcohol, and the clear liquid is poured into a watch-glass, and left to evaporate at the temperature of the air. The salicylic acid then solidifies round the edge of the glass in slender efflorescent crystals, which are pure white if the acid was previously crystallised, but more or less yellow if it was precipitated. A brownish colour indicates impurity.

For estimating the value of commercial samples of salicylic acid, Muter (*Analyst*, i, 193) uses a standard solution prepared by dissolving 1 gram of the pure acid in a litre of water, so that 1 c.c. represents 1 mgm. of acid, and an indicator liquid consisting of a solution of pure neutral ferric chloride, of such a strength that 1 c.c. added drop by drop to 50 c.c. of the standard acid just ceases to give any increase in depth of colour before the addition of the last drop or two. To perform the estimation, 1 gram of the commercial sample is dissolved in a litre of water, and 50 c.c. are put into a Nessler tube; to this 1 c.c. of ferric solution is added, and the colour observed after standing for five minutes: some of the standard acid is also poured into another tube and made up to 50 c.c. with water, and the 1 c.c. of ferric chloride added: when the colours are alike, the amount of pure acid present in the sample is equal to the amount of pure acid added: if they are not, the trial must be repeated exactly as in testing for ammonia by the Nessler process. To ensure success, the liquid should be free from mineral acids: small quantities of acetic acid likewise affect the colour at first, but it recovers itself after standing for about five minutes.

To detect the presence of salicylic acid in milk or beer, to which it is sometimes added as an antiseptic, four ounces of the liquid are dialysed for twelve hours in a pint of distilled water; if after that time salicylic acid is still found to be present by testing with ferric chloride, the dialysis must be continued for 48 hours. The amount present is then determined by the process above described.

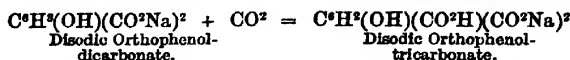
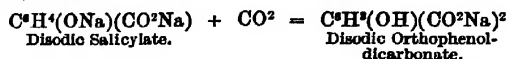
An aqueous solution of salicylic acid, mixed with a few drops of ferric chloride, is recommended by H. Weiske (*J. pr. Chem.* [2], xii, 157) as an indicator in volumetric analysis in place of litmus (the blue colour of which is very apt to change to red). To the dark violet solution thus obtained, dilute soda-solution is added to neutrality, which is known by the liquid assuming a reddish-yellow tint: This liquid being then added to the acid to be titrated with soda-solution, becomes more and more coloured as the point of neutrality is reached, but when the solution becomes alkaline the colour suddenly disappears.

Solubility.—According to H. Bosc (*Pharm. J. Trans.* [3], vi, 182), water containing 8 p. c. borax dissolves 10 p. c. of salicylic acid. The solution (which when 2-4 times diluted may be used in the treatment of wounds) is prepared by first dissolving the borax in boiling water and then adding the salicylic acid. According to T. Toussaint (*ibid.*, 263), ammonium phosphate is a better solvent for salicylic acid than sodium phosphate. Twelve parts of salicylic acid require for solution only 11 parts of ammonium phosphate. 30 grains of salicylic acid dissolve at 180° F. in an ounce of glycerin of 30° B., the greater part however separating out on cooling to 70° F.; the addition of ammonium phosphate does not prevent the separation. On the other hand, 10 grains of salicylic acid and 10 grains of ammonium phosphate dissolve in 2 drachms of glycerin and 2 drachms of water, or 16 grains salicylic acid and 16 grains phosphate in 4 drachms glycerin and 4 drachms water to a clear liquid.

Conversion into Polybasic acids.—When disodic salicylate is heated to between 300° and 400° in a current of carbon dioxide, the salicylic acid disappears, partially or entirely, and in its place a dibasic and a tribasic acid are formed, viz.:



from salicylic acid by a reaction which is analogous to, or rather a continuation of, that by which salicylic acid itself is formed when sodium-phenol is heated in a current of carbon dioxide, thus :



The action proceeds most rapidly at 370°–380°, at which temperature salicylic acid is, in the course of a few hours, completely converted into the di- and tricarboxylic acids, the latter always preponderating. These acids are insoluble in chloroform, and by means of it are easily separated from unaltered salicylic acid (Ost, *J. pr. Chem.* [2], xiv. 93).

Orthophenol-dicarbonate acid is isomeric with the oxyphthalic acid which Baeyer has obtained (*Deut. Chem. Ges. Ber.* x. 1079), by the action of nitrous acid on ethylic amidophthalate, the difference between the two doubtless depending on the orientation of the radicals OH and CO²H.

Conversion into Salicyluric acid, C⁶H³NO⁴.—The urine of fever patients who had been treated with large doses of salicylic acid was found to contain salicyluric acid, together with unaltered salicylic acid. These two acids are most readily separated by means of ether and benzene, which dissolve salicylic more readily than salicyluric acid. From an aqueous solution of the acids, the salicyluric acid crystallises out last on cooling (Piccardi, *Deut. Chem. Ges. Ber.* viii. 817).

Technical Applications of Salicylic acid.—The following depending on the antiseptic action of the acid (*2nd Suppl.*) are described by R. Wagner (*Dingl. pol. J.* cxxvii. 136). If a concentrated aqueous solution of salicylic acid be applied to fresh meat, and the meat be then placed in well-closed vessels, it will remain perfectly fresh for a long time. This solution is also very useful in the manufacture of sausages and similar foods. Butter containing a little salicylic acid will remain fresh for months even in the hottest weather. The same acid prevents the moulding of preserved fruits, and is very useful in the manufacture of vinegar.

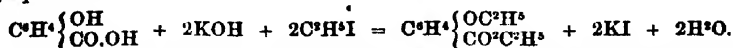
The addition of a little salicylic acid renders glue more tenacious. The acid also prevents decomposition in gut and parchment during their manufacture. Skins to be used for making leather do not undergo decomposition if steeped in a dilute solution of salicylic acid. Weaver's or bookbinder's glue, and other allied substances, may be preserved for a long time by treating them with a solution of this acid. Albumin may be preserved by the same means.

The methyl-, ethyl-, and amyl-ether of salicylic acid are used as perfumes. The calcium salt, on keeping and distilling with water, yields a liquid which has a strong odour of roses.

On the Preservation of Meat and Bread by means of Salicylic Acid, see Kolbe (*J. pr. Chem.* [2], xiii. 106; *Chem. Soc. Jour.* 1876, i. 901).

On the Antiseptic action of Salicylic Acid, see further F. Mohr (*Zeitschr. anal. Chem.* 1875, 79; *Jahresb. f. Chem.* 1875, 905; Endemann, *J. pr. Chem.* [2], xii. 260; *Jahresb.* 1875, 1111; *Chem. Soc. Jour.* 1876, i. 990; Hempel, *Deut. Chem. Ges. Ber.* viii. 1657; *Chem. Soc. Jour.* 1876, i. 711; Meyer a. Kolbe (*J. pr. Chem.* [2], xii. 178; *Chem. Soc. Jour.* 1876, i. 969).

Ethyllic Salicylate, C⁶H⁴ $\left\langle \begin{smallmatrix} \text{OH} \\ \text{CO}^2\text{C}^2\text{H}_5 \end{smallmatrix} \right\rangle$, is readily formed by passing hydrochloric acid into an alcoholic solution of the acid as long as it is absorbed. It is an oily liquid, boiling at 226°–228°, and identical with that obtained by distilling salicylic acid with a mixture of alcohol and sulphuric acid. When its potassium derivative, C⁶H⁴OK.CO²C²H⁵, is heated with ethyl iodide to 160°, the diethyl ether, C⁶H⁴(OC²C²H⁵).CO²C²H⁵, is obtained. The same compound is formed by heating salicylic acid with potash and ethyl iodide in the proportions indicated by the following equation:—



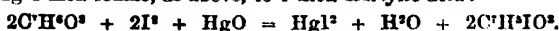
It is a colourless liquid, boiling at 160°–165°, and smelling like oil of wintergreen (C. Göttig, *Deut. Chem. Ges. Ber.* ix. 1473).

CHLOROSALICYLIC ACID, C⁶H³Cl(OH).COOH, may be prepared by passing the calculated quantity of chlorine into a mixture of salicylic acid with a large quantity of carbon sulphide. When purified by recrystallisation from water it forms small white needles melting at 172°6°.

The *barium salt*, $[\text{C}^6\text{H}^4\text{Cl}(\text{OH})\text{CO}^2]_2\text{Ba} + 3\text{H}^2\text{O}$, is freely soluble in water and alcohol, and crystallises in small needles having a splendid pearly lustre. It gives off its water at 130° , turns brown at 150° , and at 180° begins to glow and becomes carbonised. The *lead salt*, $[\text{C}^6\text{H}^4\text{Cl}(\text{OH})\text{CO}^2]_2\text{Pb}$, is a heavy crystalline precipitate. The *copper salt*, $[\text{C}^6\text{H}^4\text{Cl}(\text{OH})\text{CO}^2]_2\text{Cu}$, is an amorphous greyish-green precipitate, very slightly soluble in water. The *silver salt*, $\text{C}^6\text{H}^4\text{Cl}(\text{OH})\text{CO}^2\text{Ag}$, is a white precipitate, which blackens on exposure to light (Hübner & Brenken, *Deut. Chem. Ges. Ber.* vi. 174).

IODOSALICYLIC ACIDS (Weselsky, *Liebig's Annalen*, clixiv. 99).—The best mode of preparing these and other iodised organic acids is to add iodine and mercuric oxide alternately to a solution of the acid in alcohol of 90 per cent. The liquid becomes heated, but not above 40° ; external heating is not required.

Monoiodosalicylic acid, $\text{C}^6\text{H}^4\text{I}(\text{OH})\text{CO}^2\text{H}$, is formed (together with the di-iodated acid) by adding 1 mol. iodine, as above, to 1 mol. salicylic acid:



With 2 mols. iodine the chief product is di-iodosalicylic acid. The two acids, mono- and di-iodated, may be separated by means of their barium salts after the dissolved mercuric iodide has been removed, by evaporating the alcohol solution, and digesting the residue with solution of sodium carbonate. The mono-iodated acid exhibits two modifications [probably $\text{CO}^2\text{H} : \text{OH} : \text{I} = 1 : 2 : 4$ and $1 : 2 : 5$], one melting at 184° , the other at 196° – 198° (Fittig's *Grundriss d. org. Chemie*, p. 469), the latter being identical with the monoiodosalicylic acid described by Lautemann (v. 158). Di-iodosalicylic acid, also described by Lautemann, is a white felted mass which begins to decompose at 220° without previous fusion. The tri-iodosalicylic acid mentioned by Lautemann, Weselsky was not able to obtain. The solutions of the iodosalicylic acids are coloured violet by ferric chloride. Di-iodosalicylic acid is converted by fusion with potash into gallic acid, $\text{C}^6\text{CO}^2\text{H}\cdot\text{OH}\cdot\text{H}\cdot\text{OH}\cdot\text{OH}\cdot\text{H}$, and must therefore have a similar constitution, viz. $\text{CO}^2\text{H} : \text{OH} : \text{I} : \text{I} = 1 : 2 : 4 : 5$; hence it is probable that the two mono-iodated acids formed simultaneously with it have the formulæ $\text{CO}^2\text{H} : \text{OH} : \text{I} = 1 : 2 : 4$ and $1 : 2 : 5$; but we cannot at present say which of these two formulæ belongs to Lautemann's acid melting at 196° .

Nitroiidosalicylic acid, $\text{C}^6\text{H}^3(\text{NO}^2)_2\text{I}(\text{OH})\text{CO}^2\text{H}$, is formed by treating nitrosalicylic acid [which?] in alcoholic solution with iodine and mercuric oxide. The crude product precipitated by water and dissolved in potassium carbonate yields first the potassium salt of nitrodi-iodophenol, then that of nitroiidosalicylic acid. The *neutral potassium salt*, $\text{C}^6\text{H}^3\text{KI}(\text{NO}^2)_2\text{O}^3 + 3\text{H}^2\text{O}$, crystallises from alcohol in small orange-red needles. The less soluble *acid salt*, $\text{C}^6\text{H}^3\text{KI}(\text{NO}^2)_2\text{O}^3 + 2\text{H}^2\text{O}$, forms small orange-yellow nodules. The corresponding barium salts crystallise in bright red needles; the acid salt has the composition $[\text{C}^6\text{H}^3(\text{NO}^2)_2\text{O}^3]_2\text{Ba} + 6\text{H}^2\text{O}$ (Weselsky).

NITROSALICYLIC ACIDS, $\text{C}^6\text{H}^4(\text{NO}^2)\text{CO}^2\text{H}$ —An acid having this composition, and obtained by the action of nitric acid upon salicylic acid, salicin, and indigo, has been already described (v. 158). Two others are described by L. B. Hall (*Deut. Chem. Ges. Ber.* vii. 1320) as produced, together with the former, by the action of fuming nitric acid on salicylic acid. More recently (*ibid.* viii. 1216), H. Hübner, in whose laboratory Hall's experiments were made, mentions only the last two acids as produced by nitration of salicylic acid. These are distinguished as *ortho*- and *para*-nitrosalicylic acid, because when heated they yield respectively *ortho*- and *para*-nitrophenol. They are prepared by treating salicylic acid dissolved in glacial acetic acid with fuming nitric acid, precipitated by addition of a large quantity of water, and separated by recrystallisation, the *para*-acid separating out, while the *ortho*-acid remains in solution. If this separation does not succeed completely after the second crystallisation, the least soluble portion of the nitro-acid may be converted by boiling with dilute baryta-water into the very sparingly soluble barium salt of the *para*-acid; and on heating the filtered solutions at the boiling heat with a slight excess of barium carbonate, the salt which separates on cooling consists of barium orthonitrosalicylate very nearly pure.

Orthonitrosalicylic acid, examined specially by L. B. Hall, crystallises from water in long colourless needles, $\text{C}^6\text{H}^4(\text{NO}^2)\text{O}^3 + \text{H}^2\text{O}$, which melt at 125° ; the dehydrated acid melts at 144° – 145° . It appears also to unite with acetic acid. The aqueous solution is coloured red by ferric chloride. The following salts have been examined:—

$\text{C}^6\text{H}^4(\text{NO}^2)\text{OK}\cdot\text{CO}^2\text{K}$ crystallises from hot water in long yellow needles.

$\text{C}^6\text{H}^4(\text{NO}^2)\text{OH}\cdot\text{CO}^2\text{Ag}$ forms glistening brownish needles, easily soluble in water.

$[\text{C}^6\text{H}^4(\text{NO}^2)\text{OH}\cdot\text{CO}^2]_2\text{Ba}$ crystallises from a hot aqueous solution in scales, from dilute solutions in slender needles.

$\text{C}^6\text{H}^3(\text{NO}^2)\text{O}.\text{CO}^2.\text{O} + 3\text{H}^2\text{O}$. Yellow needles; easily soluble in hot water.

$\text{C}^6\text{H}^3(\text{NO}^2)\text{O}.\text{CO}^2.\text{Pb}$ is a yellow precipitate.

The *monethylic ether*, $\text{C}^6\text{H}^3(\text{NO}^2)\text{OH}.\text{CO}^2.\text{C}^2\text{H}^5$, obtained by heating the silver salt with ethyl iodide, separates from alcoholic solution as an oil which afterwards solidifies to light yellow prisms melting at 44° . It readily forms salts by exchange of its alcoholic hydrogen for metals. The silver salt, treated with ethyl iodide, yields the *diethylic ether*, $\text{C}^6\text{H}^3(\text{NO}^2)(\text{OC}^2\text{H}^5)_2.\text{CO}^2.\text{C}^2\text{H}^5$, as a fragrant oil slightly soluble in alcohol. Heated with alcoholic ammonia, it is converted, by exchange of $2\text{OC}^2\text{H}^5$ for 2NH^3 , into nitramidobenzamide, $\text{C}^6\text{H}^3(\text{NO}^2)\text{NH}^2.\text{CONH}^2$, which crystallises in yellow shining laminae melting at 109° .

Paranitrosalicylic acid (examined by H. Wattenberg) crystallises from water in very long, thin, colourless needles, very sparingly soluble in cold water. Its aqueous solution is coloured blood-red by ferric salts, like the ortho-acid. The following salts have been examined:—

$\text{C}^6\text{H}^3(\text{NO}^2)(\text{OH}).\text{CO}^2.\text{K}$. Reddish-yellow nodular crusts, easily soluble in water, either hot or cold.

$\text{C}^6\text{H}^3(\text{NO}^2)(\text{OH}).\text{CO}^2.\text{NH}^4$. Small, colourless, easily soluble needles.

$\text{C}^6\text{H}^3(\text{NO}^2)(\text{OH}).\text{CO}^2.\text{Ag}$. Crystallises from hot water in ramified groups of small slender reddish-yellow needles.

$[\text{C}^6\text{H}^3(\text{NO}^2)(\text{OH}).\text{CO}^2]^2\text{Ba} + 6\text{H}^2\text{O}$. Tufts of small thick yellow needles, easily soluble in cold water.

$[\text{C}^6\text{H}^3(\text{NO}^2)(\text{OH}).\text{CO}^2]^2\text{Sr} + 5\frac{1}{2}\text{H}^2\text{O}$. Groups of satiny needles which melt in their water of crystallisation at 100° – 110° ; moderately soluble in cold, easily in hot water.

$[\text{C}^6\text{H}^3(\text{NO}^2)(\text{OH}).\text{CO}^2]^2\text{Ca} + 6\text{H}^2\text{O}$ melts at 98° – 100° , and otherwise resembles the strontium salt.

$\text{C}^6\text{H}^3(\text{NO}^2).\text{O}.\text{CO}^2.\text{Mg} + 4\text{H}^2\text{O}$. Lemon-yellow crystalline nodules, very soluble in water and in alcohol.

$[\text{C}^6\text{H}^3(\text{NO}^2)(\text{OH}).\text{CO}^2]^2\text{Zn} + 5\text{H}^2\text{O}$. Broad short yellow needles easily soluble in cold water.

The *monethylic ether*, $\text{C}^6\text{H}^3(\text{NO}^2)(\text{OH}).\text{CO}^2.\text{C}^2\text{H}^5$, obtained by heating the silver salt with excess of ethyl iodide, crystallises in faintly yellowish needles often an inch long, easily soluble in alcohol and ether, melting at 92° – 93° . Its *sodium salt*, $\text{C}^6\text{H}^3(\text{NO}^2)(\text{ONa}).\text{CO}^2.\text{C}^2\text{H}^5$, crystallises in spherical groups of yellow velvety needles, easily soluble in water, less soluble in alcohol.

The *diethylic ether*, $\text{C}^6\text{H}^3(\text{NO}^2)(\text{OC}^2\text{H}^5)_2.\text{CO}^2.\text{C}^2\text{H}^5$, obtained by heating the silver salt of the monethylic ether with ethyl iodide to 125° , crystallises in small, nearly colourless needles, very easily soluble in hot water and in alcohol, melting at 98° – 99° . Heated with saturated alcoholic ammonia to 160° for eight hours, it is converted into para-nitramidobenzamide, $\text{C}^6\text{H}^3(\text{NO}^2)\text{NH}^2.\text{CONH}^2$, which forms small yellow needles melting at 140° , and is converted by boiling with barium hydrate into the barium salt of paranitramidobenzoic acid, $[\text{C}^6\text{H}^3(\text{NO}^2)(\text{NH}^2).\text{CO}^2]\text{Ba} + 4\frac{1}{2}\text{H}^2\text{O}$, which crystallises in small thick yellow needles, easily soluble in hot water. The free acid separated therefrom crystallises from water in bright yellow slender needles, moderately soluble in boiling water, also in alcohol and ether; melting at 270° .

DINITROSALICYLIC ETHERS (Salkowski, *Liebigs Annalen*, clxxiii. 43–51). *Methylic dinitrosalicylate*, $\text{C}^6\text{H}^3(\text{NO}^2)_2\text{OH}.\text{CO}^2.\text{CH}^3$, obtained by adding wintergreen oil, $[\text{C}^6\text{H}^3(\text{OH}).\text{CO}^2.\text{CH}^3]$, to a mixture of 5 pts. fuming nitric and 5 pts. fuming sulphuric acid, forms, when crystallised from alcohol, faintly yellowish scales melting at 127° – 128° .*

Methylic Ethyl-dinitrosalicylate, $\text{C}^6\text{H}^3(\text{NO}^2)_2(\text{OO}^2\text{H}^5).\text{CO}^2.\text{CH}^3$, is obtained by the action of ethyl iodide on the silver salt of the preceding acid ether, $\text{C}^6\text{H}^3(\text{NO}^2)_2\text{OAg}.\text{CO}^2.\text{CH}^3$. Considerable rise of temperature takes place, and on distilling off the excess of ethyl iodide, and treating the residue several times with hot alcohol, and leaving the filtered liquid to cool, the methylic ethyl-dinitrosalicylate separates out, and may be purified by repeated crystallisation from alcohol. From a concentrated alcoholic solution it separates at first as an oil, which, however, gradually solidifies, or may be made to solidify by throwing in a small crystal. From more dilute solutions it separates in long prismatic crystals, sometimes also in shorter, thick, highly lustrous, well-defined monoclinic prisms, having their acute lateral edges truncated, and terminated by two different pairs of augite faces. Axial ratio, $a : b : c = 1 : 0.3517 : 0.2535$. Angle $bc = 71^\circ 13'$. Observed faces, ∞P , ∞P_2 , (∞P_2) , $(P \infty)$, $2P \infty$. Melting point 80° .

This ether, heated on the water-bath with excess of ammonia, is converted into the ammonium salt of dinitro-anthranilic acid, $\text{C}^6\text{H}^3(\text{NO}^2)_2\text{NH}^2.\text{CO}^2.\text{NH}^4$ (p. 272).

* Compare v. 164, where, however, the ether is erroneously called *methyldinitrosalicylic acid*.

SALICYLIC ACID.

Dimethylic Dinitrosalicylate, or *Methylic Methylidinitrosalicylate*, $C^6H^2(NO^2)_2(OC^2H^5).CO^2CH^3$.—Prepared like the preceding, using methylic instead of ethylic iodide. Forms large thick crystals of the same form as the preceding, and melting at 69° . Ammonia converts it into dinitro-anthranilic acid.

Ethylic Dinitrosalicylate, $C^6H^2(NO^2)_2OH.CO^2C^2H^5$, prepared by passing hydrochloric acid gas into an alcoholic solution of dinitrosalicylic acid, forms colourless laminae melting at $98^\circ-99^\circ$. Its *ammonium salt*, $C^6H^2(NO^2)_2.ONH^4.CO^2C^2H^5$, crystallises in long needles having a golden lustre. The *silver salt*, $C^6H^2(NO^2)_2OAg.CO^2C^2H^5$, cannot be obtained pure by double decomposition, but is prepared by saturating the ether with the calculated quantity of finely divided silver oxide or carbonate, and heating with a large quantity of water, at first gently, and with frequent agitation, to a temperature below the melting point of the ether, afterwards to the boiling point, and filtering hot. The salt then separates in orange-coloured slender needles or in yellow spherules, both exhibiting the same composition. If any of the preceding directions are neglected, the resulting solution usually coagulates to a jelly; and the same remarkable property is exhibited by dilute solutions of silver dinitrosalicylate, whereas from concentrated solutions this salt separates in fine crystals.

Ethylic Methylidinitrosalicylate, $C^6H^2(NO^2)_2OCH^3.CO^2C^2H^5$, prepared by the action of methyl iodide on the silver salt last described, is always contaminated with an impurity, which may be removed, though with difficulty, by repeated crystallisation from very dilute alcoholic solution. From a more concentrated alcoholic solution it always separates as an oil, and even weaker solutions do not easily crystallise spontaneously, but may easily be made to crystallise by throwing in a small crystal of the same or the following (diethylic) ether; probably, therefore, the two are isomorphous.

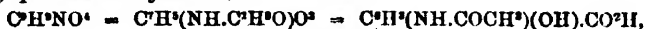
Ethylic methylidinitrosalicylate forms large, thin, colourless, six-sided tables melting at 47° . Ammonia converts it into ethylic dinitro-anthranilate.

Diethylic Dinitrosalicylate, $C^6H^2(NO^2)_2OC^2H^5.CO^2C^2H^5$, obtained by decomposing the silver salt of monethylic dinitrosalicylate with ethyl iodide, separates from concentrated alcoholic solutions as an oil, from dilute solutions in flat prismatic crystals without distinct end-faces. Melting point 40° . This ether is also converted by ammonia into ethylic dinitro-anthranilate.

AMIDOSALICYLIC ACIDS, $C^6H^2(NH^2)(OH).CO^2H$.—The hydrochloride of the ortho-acid, $C^6H^2(NH^2)O^2.HCl + H^2O$, obtained by treating orthonitrosalicylic acid with tin and hydrochloric acid, forms decomposable needles easily soluble in water. Heated with benzoyl chloride it yields fine colourless needles melting at 189° .

Paramidosalicylic acid is obtained by reducing the corresponding nitro-acid with tin and glacial acetic acid. Its *hydrochloride*, $C^6H^2(NH^2)O^2.HCl$, crystallises in small, thick, slightly brownish needles, moderately soluble in cold, freely in hot water. Its solution in hydrochloric acid, boiled with nitric acid, yields iridescent scales (chloranil?). The *sulphate*, $[C^6H^2(NH^2)O^2]^2H^2SO^4$, forms thick brownish prisms, somewhat sparingly soluble in cold, moderately soluble in hot water.

Acetyl-paramidosalicylic acid,



is obtained as a bye-product in the amidation of para-nitrosalicylic acid, and crystallises on exposing the liquid filtered from the tin sulphide to a low winter temperature, in thick colourless needles, containing $\frac{1}{2}$ mol. H^2O , moderately permanent in the air very soluble in water and in alcohol, melting at 218° .

The *magnesium salt*, $(C^6H^2NO^2)^2Mg + 8H^2O$, forms easily soluble crystalline crusts having a faint violet colour. The *barium salt*, $(C^6H^2NO^2)^2Ba + 4H^2O$, crystallises in small reddish needles grouped in rosettes, easily soluble in cold, very easily in hot water. The *calcium salt*, $(C^6H^2NO^2)^2Ca + 5\frac{1}{2}H^2O$, forms groups of thin colourless needles, sparingly soluble in cold, easily in hot water. The *zinc salt*, $(C^6H^2NO^2)^2Zn + 10H^2O$, crystallises in felted groups of small slender needles easily soluble in water, either hot or cold (Wattenberg, *Deut. Chem. Ges. Ber.* viii. 1215).

Salicylanilide, $C^6H^4NO^2 = C^6H^4(OH)-CO.NH.C^6H^5$ (R. Wanstrat, *Deut. Chem. Ges. Ber.* vi. 33).—This compound is formed by dropping phosphorus trichloride into a mixture of aniline and salicylic acid. The product when cold forms a yellowish brittle mass, which may be freed from phosphorous acid, hydrochloric acid, and aniline hydrochloride by boiling with water, and further purified by crystallising it, first from alcohol, with addition of animal charcoal, and then several times from water. It is thus obtained in small white prisms melting at $134^\circ-135^\circ$. It is not attacked by dilute acids, but dilute alkalis cause it to split up into aniline and salicylic acid. When fused with barium hydrate it yields phenol and aniline. It dissolves in sulphuric acid, and is reprecipitated by water. Its alcoholic solution strikes a violet colour with ferric chloride.

Salicylnitrilanide, $C^6H^4OH - CO(NH.C^6H^4NO_2)$, obtained in like manner with nitraniline and salicylic acid, crystallises from alcohol in groups of needles melting at $217^{\circ}-218^{\circ}$, and reacts with acids, alkalis, and ferric chloride, like salicylanilide.

Salicyl-toluidide, $C^6H^3NO_2 = C^6H^4OH - CO[NH.C^6H^4(CH^3)]$, is obtained by the action of phosphorus trichloride on a mixture of toluidine and salicylic acid; it is not easy to prepare, as secondary products are formed to a considerable extent. It crystallises in white prisms melting at $155^{\circ}-156^{\circ}$, and when boiled with aqueous potash splits up into toluidine and salicylic acid. On fusion with barium hydrate it yields phenol and toluidine. It is far less soluble in water than the salicylanilide, but behaves like that substance with other solvents (Wanstrat).

(2). **Metaoxybenzoic**, or simply **Oxybenzoic Acid**, $C^6.OO^2H.H.OH.H^2$. This acid is formed, together with a smaller quantity of salicylic acid (1 : 2), when chlorosalicylic (ortho-chlorobenzoic) acid, is fused with potassium hydrate. The largest proportion of the meta-acid is obtained when 1 pt. of chlorosalicylic acid is fused with 2 to $2\frac{1}{2}$ pts. of pulverised potassium hydrate in a retort placed in an oil-bath at 150° . The reaction begins at this temperature, and soon becomes so violent as to render it necessary to remove the retort repeatedly from the oil-bath. The cessation of the frothing indicates the complete decomposition of the chlorosalicylic acid. The thermometer then exhibits the constant temperature of 200° . Subsequent raising of the temperature to 250° does not alter the products. On dissolving the melt in hot water and acidulating, there remains an amorphous nearly insoluble body of unknown composition; and the aqueous solution contains the oxybenzoic and salicylic acids, which may be extracted from it by ether, and separated by means of chloroform, which readily dissolves the latter. From 45 grams of chlorosalicylic acid thus treated there were obtained 10.5 oxybenzoic and 5 salicylic acid. If the action of the potash be allowed to go on violently, the proportion of salicylic acid obtained is less. The contrary is the case in fusing with sodium hydrate (2 pts. NaHO to 1 pt. chlorosalicylic acid); in this case the action goes on much more quietly, and the quantities of the two acids obtained are nearly equal. Increase of the quantity of potassium hydrate or addition of potassium carbonate has no influence on the result. But if 1 mol. of the acid be fused with 2 mols. potassium or sodium hydrate, the reaction is extremely violent, and only small quantities of the two oxy-acids are obtained. Paraoxybenzoic acid has not been observed in either case (Ost, *J. pr. Chem.* [2], xi. 385).

Oxybenzoic acid when distilled passes over for the most part unchanged, but at the same time acquires a yellow colour, due to the presence of 1 or 2 per cent. of anthraflavone, $C^{14}H^{10}O^4$, formed from it by dehydration and condensation: $2C^6H^4O^2 - 2H^2O = C^{14}H^{10}O^4$. This change takes place to a much greater extent on heating the oxybenzoic acid with strong sulphuric acid (Barth a. Senhofer). See ANTHRAFLAVONE (p. 107).

Iodoxybenzoic acid, $C^6H^3I(OH).CO^2H$, is formed, together with di-iodophenol, by alternately adding iodine and mercuric oxide to oxybenzoic acid dissolved in alcohol of 90 per cent., the quantity of di-iodophenol increasing with the proportion of iodine employed. The two compounds are separated by boiling water, which leaves the greater part of the di-iodophenol undissolved. Iodoxybenzoic acid forms small needles mostly united in groups slightly soluble in cold, very soluble in boiling water. *Di-iodoxybenzoic acid* has not been obtained.

Nitro-iodoxybenzoic acid, $C^6H^3I(NO^2)O^2$, prepared in like manner from nitro-oxybenzoic acid, forms small lemon-yellow crystals, sparingly soluble in water, easily in hot alcohol. The acid barium salt, $[C^6H^3I(NO^2)O^2]_2Ba + 6H^2O$, crystallises in microscopic needles of a deep roseate colour (Weelsky, *Liebigs Annalen*, clxiv. 99).

(3). **Paraoxybenzoic Acid**, $C^6.CO^2H.H.H.OH.H^2$. **Formation**—1. From Phenol. When carbon dioxide is passed through a solution of potassium in boiling phenol, paraoxybenzoic acid is produced, in the same manner as salicylic acid is formed by treating phenol with carbon dioxide and sodium (v. 152; 2nd Suppl. 1065):

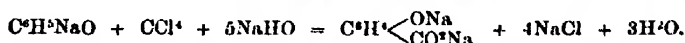


The paraoxybenzoic acid, separated from the resulting potassium salt, always contains a little salicylic acid, probably due to a small quantity of sodium contained in the potassium. The two acids may be separated by boiling chloroform, which dissolves salicylic acid freely and paraoxybenzoic acid but sparingly (Kolbe, *J. pr. Chem.* [2], viii. 336).

To obtain a good yield of paraoxybenzoic free from salicylic acid, special precautions are, however, required. The following process is described by Hartmann (*ibid.* xvi. 35). Potassium phenate is first prepared by adding solid potassium hydrate to phenol heated in a shallow iron basin; the mixture is evaporated at a rather high

temperature, and with constant stirring, till the mass begins to separate in small nodules; the heat is continued for a few minutes longer; and the flame then suddenly removed. If the heating be discontinued too soon, the potassium phenate retains moisture, and then yields but a small quantity of para-oxybenzoate when treated with carbon dioxide; and if it be too much prolonged, violent decomposition of the potassium phenate is likely to ensue. For the preparation of large quantities, an iron retort provided with a stirring apparatus is required. In a well conducted operation, the quantity of paroxybenzoic acid (separated from the potassium salt by hydrochloric acid) should be about 80 per cent. of the potassium phenate used.

Paraoxybenzoic acid is also formed, together with salicylic acid, by heating phenol in an alcoholic solution containing excess of potash or soda, with carbon tetrachloride:



The same reaction takes place, though less quickly, in aqueous solution. Good proportions are: 28 pts. NaHO, or 36KHO, dissolved in a small quantity of boiling water, and so much alcohol that carbon tetrachloride produces no turbidity in the liquid, together with 10 pts. of crystallised phenol, and 17 pts. CCl_4 , the mixture being heated to 100° in sealed tubes for two or three days. The relative quantities of paraoxybenzoic and salicylic acids produced do not appear to be affected by the nature of the alkali employed (Reimer & Tiemann, *Deut. Chem. Ges. Ber.* ix. 1286).

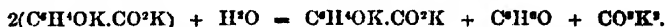
2. From Salicylic Acid.—Monopotassic salicylate heated to 220° is resolved into phenol, carbon dioxide, and dipotassic paraoxybenzoate, according to the equation:



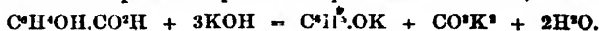
Monosodic salicylate similarly treated yields disodic salicylate.

The paraoxybenzoate thus formed is tolerably pure if the air has been excluded during the process: otherwise the paraoxybenzoic acid separated from it is dark-coloured; but even then it is easily purified and obtained as a snow-white mass by recrystallisation with the aid of animal charcoal. Tetraethylammonium salicylate likewise yields paraoxybenzoic acid when heated; but the barium, strontium, and calcium salts, and, indeed, all the other salicylates hitherto tried, behave like the sodium salt, yielding not paraoxybenzoates, but dimetallic salicylates (Kolbe, *J. pr. Chem.* xi. 249; Ost, *ibid.* 385).

Dipotassic salicylate acts precisely like the monopotassic salt, yielding dipotassic paraoxybenzoate, potassium carbonate, and phenol: thus



A mixture of salicylic acid and 3 mols. of potash, acts quite differently from the dipotassic salt; at 250° no change ensues, but at 300° every trace of salicylic acid becomes converted into potassium-phenol and potassium carbonate, thus—



The same result occurs if the monopotassic salt and 2 mols. of caustic potash or the dipotassic salt and 1 mol. are heated together. When, however, 4 or more molecules of potash are employed, little or no change takes place at 300° , and in no case is paraoxybenzoic acid produced. In order, therefore, to obtain paraoxybenzoic acid from salicylic acid, not more than 2 mols. of potash to 1 of acid must be used; with $2\frac{1}{2}$ mols. some paraoxybenzoic acid is formed, but most of the salicylic acid splits into phenol and carbonic acid.

The non-formation of paraoxybenzoic acid with soda and with more than 2 mols. of potash is not due to the convertibility of paraoxybenzoic acid into salicylic acid under these conditions: for on heating paraoxybenzoic acid to various temperatures with different proportions of potash and of soda, it is found that, in the former case, smaller quantities of alkali than 6 mols. bring about more or less decomposition into phenol and carbonic acid, but 6 mols. or more entirely prevent this decomposition at 300° ; with soda, 4 mols. completely stop this change, which is readily undergone by the mono- and disodic salts. In no case is either oxybenzoic or salicylic acid produced.

In this case, therefore, as in many others, potash and soda differ materially in their action when fused with organic bodies. Moreover the nature of the change varies with the temperature, and especially with the proportion of alkali employed; and these circumstances may perhaps throw some light on the discordant results obtained by different chemists in heating one and the same phenol-derivative with caustic alkali, the same chlorophenol, for example, sometimes yielding resorcin and sometimes hydroquinone. Such variations might indeed arise from the use of potash

containing more or less soda. Hence it is plain that fusion with caustic alkalis cannot be safely used as a means of determining the orientation of the lateral chains in benzeno-derivatives (Kolbe, *J. pr. Chem.* [2], x. 89, 451; Ost, *ibid.* xi. 385).

3. From *Tyrosine*. This compound, fused with twice its weight of sodium hydrate, yields sodium paraoxybenzoate, together with ammonia and hydrogen (Ost, *J. pr. Chem.* [2], xii. 159).

Paraoxybenzoic acid crystallises in monoclinic prisms (iv. 353). Measurements of the angles by von Reusch are given in Hartmann's paper above cited.

The following salts, prepared by neutralising the hot aqueous solution of the acid with the corresponding carbonates, have been examined by Hartmann.

The *ammonium*, *potassium*, and *sodium salts* crystallise from concentrated solutions at low temperatures. The solution of the ammonium salt gives off ammonia during evaporation, and must therefore be kept neutral by addition of ammonia.

$\text{C}^6\text{H}^4\text{OH.CO}^2\text{NH}^4 + \text{H}^2\text{O}$ forms slowly efflorescent prisms an inch long.— $\text{C}^6\text{H}^4\text{OH.CO}^2\text{K} + 3\text{H}^2\text{O}$ forms non-efflorescent crystals, and does not give off the whole of its water even over sulphuric acid in a vacuum.— $\text{C}^6\text{H}^4\text{OH.CO}^2\text{Na} + 5\text{H}^2\text{O}$. Translucent tablets having a slight brown colour and very efflorescent.

$(\text{C}^6\text{H}^4\text{OH.CO}^2)^2\text{Ca} + 4\text{H}^2\text{O}$. Slender needles.

$(\text{C}^6\text{H}^4\text{OH.CO}^2)^2\text{Ba} + 2\text{H}^2\text{O}$. Flat shining needles or crystalline mass, apparently composed of acute rhombohedrons with basal pinacoid.

The *strontium salt* was once accidentally obtained in rather large crystals, usually in slender needles.

$(\text{C}^6\text{H}^4\text{OH.CO}^2)^2\text{Cd}$.—Separates from hot strong solutions in fine needles with $4\text{H}^2\text{O}$ (iv. 353); from the mother-liquor, after some time in crystals with $6\text{H}^2\text{O}$.

$(\text{C}^6\text{H}^4\text{OH.CO}^2)^2\text{Zn} + 8\text{H}^2\text{O}$.—Broad laminar crystals (Hlasiwetz a. Barth, *Liebig's Annalen*, cxxiv. 272); granular crystals (Hartmann).

The *ethylic ether*, $\text{C}^6\text{H}^4\text{OH.COOC}^2\text{H}^3$, prepared in the usual way by passing hydrogen chloride into the alcoholic solution of the acid, is a crystalline mass which melts when heated under water, and dissolves to a small amount in boiling water. It is nearly insoluble in carbon sulphide, sparingly soluble in chloroform and benzine, very soluble in alcohol and ether. It melts at 116° . Ammonia dissolves it readily, without however producing any perceptible alteration in it, even after a considerable time.

Paraoxybenzamide, $\text{C}^6\text{H}^4\text{OH.CONH}^2$, is obtained by heating the ether under pressure with highly concentrated aqueous ammonia. On evaporating the product over the water-bath, the excess of ammonia escapes, and the undecomposed ether then separates as a heavy liquid, from which the aqueous solution may be decanted. This solution, when strongly concentrated, yields the amide on cooling in slender brownish needles, which may be decolorised by animal charcoal, and freed from traces of the ether by treatment with chloroform.

The pure amide crystallises from aqueous solution by rapid cooling in capillary needles; by slow cooling in thicker, highly lustrous needles, often 3–4 c.m. long, with rhombic cross-section. They contain 1 mol. H^2O , which is given off quickly at 100° , slowly over sulphuric acid. The compound dissolves easily in alcohol and in hot water, sparingly in ether and in cold water, and is nearly insoluble in chloroform, carbon sulphide and benzine. It melts at 162° . Its aqueous solution has a faint acid reaction. Heated with caustic potash, it gives off ammonia, and yields potassium paraoxybenzoate.

Paraoxybenzamide possesses both basic and acid properties, the latter being due to the hydroxyl which it still retains. Its *sodium salt*, $\text{C}^6\text{H}^4\text{ONa.CO}^2\text{NH}^2$, separates as a thick white precipitate on mixing a cold alcoholic solution of the amide with aqueous soda, and may be obtained pure by removing the excess of the amide with ether, and drying it in a stream of hydrogen. In the moist state it is decomposed by the carbonic acid of the air. It dissolves easily in water and in alcohol, but is insoluble in ether. From the alcoholic solution it separates on evaporation over sulphuric acid as a crystalline mass. From the aqueous solution acids reprecipitate the amide.

The *hydrochloride*, $\text{C}^6\text{H}^4\text{OH.CONH}^2 + \text{HCl}$, obtained by passing dry hydrogen chloride over the amide contained in a Liebig's drying tube, is a solid body, which melts at 205° – 206° , and dissolves in water, but is decomposed when heated therewith with reproduction of the amide.

Paraoxybenzamide appears also to form a well-crystallised compound with *nitric acid* (Hartmann).

Paraoxybenzonitril, or *Paracyanophenol*, $\text{C}^6\text{H}^3\text{NO} = \text{C}^6\text{H}^3\text{<}\begin{smallmatrix} \text{OH} \\ \text{CN} \end{smallmatrix}$, is formed from the amide, or better from ammonium paraoxybenzoate, by rapid distillation with phosphoric anhydride, and collects in the receiver as a heavy oil mixed with

phenol, from which it may be freed by boiling with water, till the odour of phenol is no longer perceptible and the oil itself is dissolved. The filtered solution on cooling deposits the nitril in thin rhombic laminae having a splendid iridescence. It has a sweet taste, with biting after-taste; dissolves slightly in cold, more freely in hot water, but without combining therewith; dissolves also in alcohol, ether, and chloroform. Melts at 113° .

The nitril boiled with caustic alkalis gives off ammonia, and is converted into a paraoxybenzoate. It also takes up water when boiled with hydrochloric acid, and the solution on cooling deposits slender needles of the above-described hydrochloride of paraoxybenzamide. Like the amide, it also forms a *sodium salt*, $C^6H^4ONa.CN$, which is precipitated on adding aqueous soda-ley not in excess to a cold ethereal solution of the nitril. It is moderately soluble in water, and separates therefrom in crystals containing $3H^2O$.

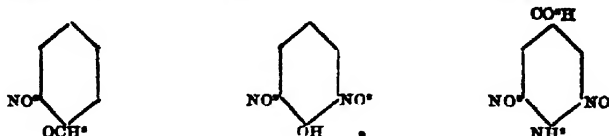
This nitril closely resembles the metacyanophenol discovered by Griess, but has only a slight resemblance to Limpricht's so-called *salicylimide* (166).

Iodoparaoxybenzoic acids, mono- and di-, are produced by alternately adding iodine (1 or 2 mols.) and mercuric oxide to a solution of paraoxybenzoic acid in alcohol of 90 per cent. Tri-iodophenol (formerly mistaken for tetraiodosalicylic acid) is formed at the same time (Weselsky, *Liebigs Annalen*, clxiv. 90). The mono- and di-iodated acids thus prepared agree in all their characters with those described by Peltzer (1st Suppl. 900).

Nitroiodo-paraoxybenzoic acid, $C^6H^4I(NO^2)O^2$, formed in like manner from nitro-paraoxybenzoic acid, forms lemon-yellow light needles. The *neutral barium salt*, $C^6H^4I(NO^2)O^2Ba + 2H^2O$, crystallises in short cinnabar-red needles with green metallic lustre; the *acid barium salt*, $[C^6H^4I(NO^2)O^2]^2Ba + 4H^2O$, in shining, roseate, flat needles and tablets. The formation of this acid is accompanied by that of paradi-iodonitrophenol, the potassium salt of which, $C^6H^4KI^2(NO^2)O^2$, is the first to crystallise out (Weselsky).

Dinitromethylparaoxybenzoic acid, or *Dinitranisic acid*, $C^6H^4(NO^2)_2(OCH^3).COOH$ (Salkowsky a. Rudolph, *Deut. Chem. Ges. Ber.* x. 1254).—This acid may be conveniently prepared by adding pure nitranisic acid (m. p. 189°) in portions of 40 grams to a well-cooled mixture of 140 grams of nitric acid, sp. gr. 1.5 and 160 grams of strong sulphuric acid. The greater part of the dinitranisic acid separates from the liquid in slender needles in the course of 48 hours, and may be collected in a funnel stopped with a cone of platinum. An additional quantity may be obtained from the filtrate, together with di- and trinitranisol, by addition of water. The dinitranisic acid, purified by solution in cold dilute solution of sodium carbonate, reprecipitation, and recrystallisation from dilute alcohol, melts at 181° – 182° .

Dinitranisic acid, heated to 160° for five hours with 5 parts of water, is converted into dinitroparaoxybenzoic acid, which separates in plates, and methyl alcohol; and if the heating be prolonged and the temperature raised to 170° , the tabular crystals likewise disappear, being resolved into CO^2 , which escapes on opening the tube, and a crystalline mass, which melts much below the boiling point of water. On dissolving this mass in dilute sodium carbonate, and leaving the solution to crystallise, fine red needles are obtained, consisting of the sodium derivative of β -dinitrophenol (2nd Suppl. 927). Now, as anisic acid belongs to the para-series, and β -dinitrophenol has its two NO^2 -groups contiguous to the hydroxyl, it follows that dinitranisic, dinitroparaoxybenzoic, dinitroparamidobenzoic (chrysanisic) acid, &c., must have the constitution 1 : 3 : 4 : 5 (CO^2 in 1), thus—

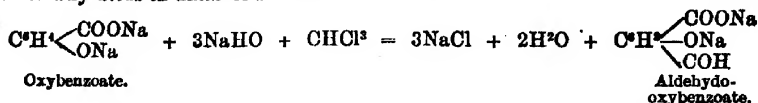


Mononitranisic acid, $C^6H^4.CO^2H.H.NO^2.OCH^3.H^2$, heated with water under pressure, should yield, in like manner, nitroparaoxybenzoic acid and orthonitrophenol; the latter is however the sole product actually obtained, whence it would appear that the temperature at which the nitranisic acid is saponified suffices also for the decomposition of the nitroparaoxybenzoic acid into CO^2 and orthonitrophenol. The decomposition may accordingly be represented by the following equation:



Aldehyde-oxybenzoic Acids, $C^6H^4O^4 = C^6H^3 \begin{matrix} \swarrow COOH \\ \downarrow OH \\ \searrow COH \end{matrix}$ (Reimer a. Tiemann,

Deut. Chem. Ges. Ber. ix. 1268). These acids, intermediate in character between oxy-acids and aldehydes, are produced, like salicylic aldehyde, by the action of chloroform on oxy-acids in alkaline solution :



In this manner two aldehyde-acids have been obtained from salicylic, and one from paraoxybenzoic acid.

a. When pure salicylic acid (14 parts) and solid sodium hydrate (25 parts), dissolved in water (50 parts) are boiled with chloroform (15 parts) for some hours, and the product of the reaction is dissolved in water and strongly acidified with hydrochloric acid, a yellow precipitate is thrown down, which dissolves readily in ether, and is taken up therefrom almost entirely by an aqueous solution of acid sodium sulphite. The latter solution, when boiled with dilute sulphuric acid, deposits a crystalline precipitate, separable by crystallisation from water into the two following bodies :—

(1). *Paraldehydosalicylic acid*, ($CO^2H : OH : COH = 1 : 2 : 5$).—This acid crystallises out in long delicate yellowish needles, melting when pure at 248° – 249° , and dissolving freely in ether and hot alcohol, but very sparingly in water and chloroform. The aqueous solution produces a deep cherry-red coloration with ferric chloride. It decomposes carbonates with effervescence, and combines with acid sodium sulphite, thus behaving both as an acid and an aldehyde. Its calcium salt, submitted to dry distillation with calcium hydrate, yields paraoxybenzoic aldehyde; whence it may be inferred that the aldehyde-group occupies the para-position in relation to the hydroxyl.

(2). *Orthoaldehydosalicylic acid*, ($CO^2H : OH : COH = 1 : 2 : 3$).—This body is contained in the mother-liquor of the preceding, and is taken up therefrom by ether, which leaves it on evaporation in the form of a white crystalline mass. When pure, it crystallises in delicate needles, which melt at 166° , and sublime without decomposition at a somewhat higher temperature. Its aqueous solution is coloured yellow by soda, and red by ferric chloride. It decomposes carbonates with effervescence, and combines with acid sodium sulphite, like the preceding compound. Its calcium salt, distilled with calcium hydrate, yields pure salicylic aldehyde, showing that the aldehyde-group occupies the ortho-position in relation to the hydroxyl.

β . Paraoxybenzoic acid, treated in a precisely similar manner with chloroform and sodium hydrate, yields only one aldehyde-acid, together with paraoxybenzoic aldehyde. On diluting the product of the reaction with 6 to 8 parts of water, acidulating with hydrochloric acid, extracting the organic products with ether, agitating the ethereal solution with acid sodium sulphite, separating the aqueous liquid from the ether, mixing it with a slight excess of dilute sulphuric acid, and passing steam into the liquid till all the liberated sulphurous acid is expelled, aldehyde-paraoxybenzoic acid crystallises out in needles, the quantity of which increases considerably as the liquid cools, and paraoxybenzaldehyde remains in solution.

Aldehyde-paraoxybenzoic acid, ($CO^2H : COH : OH = 1 : 3 : 4$), crystallises in thin yellow prisms, melts at 243° – 244° , and sublimes in long white needles at a somewhat higher temperature. It dissolves sparingly in chloroform and water, easily in alcohol and ether. The aqueous solution is coloured yellow by soda, and brick-red by ferric chloride. It decomposes carbonates with effervescence, and combines with acid sodium sulphite. Its calcium salt, submitted to dry distillation, yields salicylic aldehyde, and a small quantity of phenol, showing that the aldehyde residue and the hydroxyl-group occupy the same positions as in salicylic aldehyde.

Dioxybenzoic Acids, $C^6H^4O^4 = C^6H^3(OH)^2.COOH$. Of the six possible acids of this group, four are known, viz. oxysalicylic acid, protocatechuic acid, and two acids formed by the action of melting potash on the corresponding disulphobenzoic acids (p. 297). The constitution of the last three of these acids has been discussed in *2nd Suppl.* p. 432; that of oxysalicylic acid is determined by its formation from iodosalicylic acid. The following is a comparative view of the origin, constitution, and characteristic properties of these four acids :—

Formula	Origin	M. P.	Reaction with $\text{Fe}^{+3}\text{Cl}^{-}$
Dioxybenzoic acid 1 : 2 : 3 or 1 : 3 : 6	From corr. disulphobenzoic acid	222°	Not coloured
Dioxybenzoic acid 1 : 2 : 4	From (1 : 2 : 4) $\text{C}^6\text{H}^3(\text{SO}^3\text{H})^2.\text{CO}^2\text{H}$ and (1 : 2 : 4) $\text{C}^6\text{H}^3(\text{SO}^3\text{H})^2.\text{CH}^3$	148° (hyd.) 194° (anhyd.)	Dark rose-red
Protocatechuic acid (1 : 3 : 4)	From iodo- <i>p</i> -oxybenzoic acid, &c.	199°	Green, changed by dilute Na^+CO^3 to blue, then red
Oxysalicylic acid (1 : 2 : 5)	From iodosalicylic acid	196°-197°	Deep blue, changed to red, then brown by NH^3 or Na^+CO^3

Oxysalicylic or Hydroquinone Carbonic Acid, $\text{C}^6\text{H}^2(\text{OH})_2.\text{H}.\text{H}.\text{OH}.\text{H}.$ This acid prepared by fusing bromo- or iodosalicylic acid with potash, melts, according to Rakowski a. Leppert (*Deut. Chem. Ges. Ber.* viii. 788, 976) at 196°-197°. This agrees nearly with the statement of Lautemann, who found the acid to melt at 193° (iv. 320). According to Demole (*ibid.* vii. 1436) it melts at 183°. Heated in a sulphuric acid bath to 215°, it yields a sublimate of pure hydroquinone (showing that its two HO-groups are in the para-position), but when it is heated in a retort over an open fire, the hydroquinone is accompanied by a small quantity of pyrocatechin. Heated with weak oxidising agents it yields a crystallisable acid (quinone-carbonic acid?) which may be extracted with ether, and is instantly decolorised by reducing agents.

Protocatechuic Acid, $\text{C}^6\text{H}^3(\text{OH})_2.\text{H}.\text{H}.\text{OH}.\text{H}.$ This acid is formed: a. From potassium cresylsulphonate (ii. 108), by fusion with potash (Biedermann, *Deut. Chem. Ges. Ber.* vi. 326). β . In like manner from vanillin (Tiemann a. Haarmann, *ibid.* vii. 608); and γ . from hydropiperic acid, $\text{C}^{12}\text{H}^{12}\text{O}^4$ (Paternò a. Fileti, *ibid.* 81).

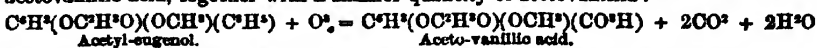
On the preparation of Protocatechuic acid from Kino, and its resolution by Bromine into CO^2 and Tetrabromopyrocatechin, see 2nd Suppl. 1023.

By heating it to 100° with a saturated solution of chlorine in carbon tetrachloride, Stenhouse obtained a chlorinated compound, which, after crystallisation from carbon sulphide, formed colourless needles (*Chem. News*, xxix. 95).

Methyl-protocatechuic acid, $\text{C}^6\text{H}^3\text{O}^4 = \text{C}^6\text{H}^3(\text{OH})(\text{OCH}^3)(\text{COOH})$.—Of this acid two modifications are known, one of which is identical with vanillic acid; the other may be called isovanillic acid.

a. Vanillic acid, $(\text{CO}^2\text{H} : \text{OCH}^3 : \text{OH} = 1 : 3 : 4)$, is produced: (1). In small quantity from vanillin (its aldehyde) by the action of various oxidising agents, most readily by exposing moist and finely pulverised vanillin to the air. (2). It is more easily prepared by mixing a warm solution of *coniferin*, $\text{C}^{16}\text{H}^{22}\text{O}^8$ (v. 1201), in 30-40 pts. water with a solution of 2 to 3 pts. potassium permanganate in 60 to 90 pts. water, filtering or straining from the precipitated hydrate of manganese dioxide, acidulating with sulphuric acid, warming the liquid for a short time to 60°-75°, and then shaking it with ether.

(3). From *Eugenol*, $\text{C}^8\text{H}^7(\text{OH})(\text{OCH}^3)\text{C}^6\text{H}^5$.—Acetyl-eugenol, subjected to the action of oxidising agents in a slightly acid solution, yields a large quantity of acetovanillic acid, together with a smaller quantity of acetovanillin:



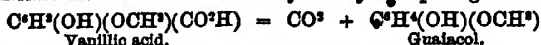
and these bodies heated with potash yield respectively vanillic acid and vanillin (Tiemann, *Deut. Chem. Ges. Ber.* ix. 52).

Vanillic acid crystallises from ether as a laminar mass of pure white colour. It dissolves very easily in alcohol, less readily in ether, sparingly in cold, more freely in hot water, from which it separates on cooling in white translucent needles. It smells like vanilla, especially when heated; melts at 211°-212° (uncorr.), and sublimes without decomposition. It gives no reaction with ferric chloride. By heating to 100°-150° with hydrochloric acid, it is resolved into protocatechuic acid and methyl chloride; yields protocatechuic acid also when fused with potash. By heating it to 140° for several hours with 2 mols. CH^3I and 2 mols. KOH , and saponifying the resulting ether, dimethylprotocatechuic acid is obtained, melting at 174° (uncorr.) (Tiemann, *ibid.* viii. 609 and 1123).

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Calcium vanillate distilled with calcium hydrate yields pure guaiacol :



Acetovanillic acid, $\text{C}^6\text{H}^3\text{O}^4 = \text{C}^6\text{H}^3(\text{OC}^2\text{H}^3\text{O})(\text{OCH}^3)(\text{CO}^2\text{H})$, is obtained by prolonged digestion of vanillic acid with acetic anhydride at 100° , and precipitation with water. It is sparingly soluble in hot water, easily in alcohol and ether, and crystallises most readily from dilute alcohol in slender colourless needles, melting at 142° (uncorr.) By boiling with potash, it is resolved into vanillic and acetic acids (Tiemann a. Nagajosi Nagai, *Deut. Chem. Ges. Ber.* viii. 1142).

Nitracetovanillic acid, $\text{C}^6\text{H}^3(\text{NO}^2)\begin{matrix} \text{OCH}^3 \\ \text{OC}^2\text{H}^3\text{O} \\ \text{COOH} \end{matrix}$, is formed by the action of nitric acid

on acetovanillic acid. It crystallises in colourless needles, which melt at 181° – 182° with partial decomposition.

Nitrovanillic acid, $\text{C}^6\text{H}^3(\text{NO}^2)\begin{matrix} \text{OCH}^3 \\ \text{OH} \\ \text{COOH} \end{matrix}$.—This body cannot be obtained by the

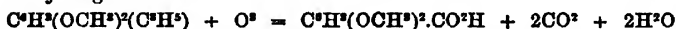
direct action of nitric acid on vanillic acid. It is formed, together with sodium acetate, by heating the preceding compound with dilute soda-ley. It forms white glistening needles, which decompose without melting at 210° . Its sodium-salt crystallises in yellow needles (Tiemann a. Matsumoto, *ibid.* ix. 937).

β . *Isovanillic acid* ($\text{CO}^2\text{H} : \text{OH} : \text{OCH}^3 = 1 : 3 : 4$) is formed by heating protocatechuic acid with potash and methyl iodide; also by heating hemipinic acid to 100° with strong hydrochloric acid; and, together with vanillic acid, by digesting dimethyl-protocatechuic acid for several hours at 140° with very dilute hydrochloric acid. The two acids may be separated by crystallisation from hot water, vanillic acid being much the more soluble of the two. Isovanillic acid melts at 250° (Tiemann).

Dimethylprotocatechuic acid, $\text{C}^6\text{H}^3\text{O}^4 = \text{C}^6\text{H}^3(\text{OCH}^3)^2\text{CO}^2\text{H}$.—This acid, originally obtained by heating protocatechuic acid (1 pt.) with methyl iodide (4 pts.) and potassium hydrate (1 pt.) dissolved in methyl alcohol (2nd Suppl. 431), is also produced by the oxidising action of potassium permanganate: α . On methyl-cresol (trimethyl-pyrocatechin):



β . On methyl-eugenol :



(Tiemann a. Mendelsohn, *Deut. Chem. Ges. Ber.* viii. 1136; Tiemann a. Matsumoto, *ibid.* ix. 937).

Nitrodimethylprotocatechuic acid, $\text{C}^6\text{H}^3(\text{NO}^2)(\text{OCH}^3)^2\text{COOH}$, is obtained by warming dry dimethylprotocatechuic acid with nitric acid of sp. gr. 1.25 till the first violent action is over. On addition of water, a yellow flocculent mass is thrown down, from which the acid is extracted by ammonia, indifferent products remaining undissolved. The acid, when pure, crystallises in yellow needles containing $\frac{1}{2}$ mol. of water, easily soluble in alcohol, ether, and hot water. The ammonium salt, $\text{C}^6\text{H}^3(\text{NH}^4)\text{NO}^2$, crystallises in pale-yellow needles, easily soluble in water and sparingly in alcohol. It loses ammonia at 100° . The silver salt, $\text{C}^6\text{H}^3\text{AgNO}^2$, is a pale-yellow precipitate, which dissolves in boiling water and crystallises in fine pale-yellow needles. It is stable and does not blacken in the light. The ethyl compound, $\text{C}^6\text{H}^3(\text{C}^2\text{H}^5)\text{NO}^2$, is formed by saturating with dry hydrogen chloride a solution of the acid in absolute alcohol, distilling off excess of alcohol, and adding water, when the ethyl-compound is thrown down as a yellow oil, which afterwards solidifies. It crystallises from weak spirit in nacreous flat prisms, which melt at 99° – 100° and dissolve in alcohol and ether.

When a solution of nitrodimethylprotocatechuic acid in hot water is treated with tin and hydrochloric acid, the liquid, on cooling, deposits crystals of a double-salt of stannous chloride and amidodimethylprotocatechuic hydrochloride :

Amongst the indifferent bodies formed by the action of nitric acid on dimethyl-protocatechuic acid are the following, which have been isolated and analysed :—

1. *Mononitrodimethylpyrocatechin*, $\text{C}^6\text{H}^3(\text{NO}^2)(\text{OCH}^3)^2$, crystallises in fine yellow needles, which melt at 95° – 96° , and dissolve sparingly in water, easily in alcohol and ether.

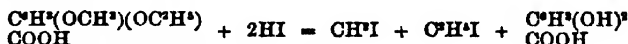
2. *Trinitrodimethylpyrocatechin*, $\text{C}^6\text{H}^3(\text{NO}^2)^3(\text{OCH}^3)^2$, crystallises in white glisten-

ing prisms, which melt at 144° – 145° , and dissolve in hot alcohol and ether (Tiemann a. Matsumoto).

Veratric acid, a constituent of *sabadilla* seeds (v. 995), is identical with dimethylprotocatechuic or methylvanillic acid, inasmuch as it is converted by fusion with potash into protocatechuic acid, and when heated with hydriodic acid to 150° – 180° it yields methyl iodide and protocatechuic acid, together with a small quantity of another acid, which, when again heated with hydriodic acid to 170° , yields CHI , CO^2 , and pyrocatechin.

By treating protocatechuic acid (from oil of cloves) with sodium methylate and methyl iodide, the methylic ether of dimethylprotocatechuic acid, $\text{C}^6\text{H}_4(\text{OCH}^3)^2\text{CO}^2\text{CH}^3$, is obtained in colourless needles melting at 58° , and having a pleasant but faint aromatic odour. On saponifying this ether with potash-ley, and adding hydrochloric acid, dimethylprotocatechuic acid is obtained in needles melting at 179.5° , and exhibiting all the properties of veratric acid (Koerner, *Gazz. chim. ital.* vi. 142).

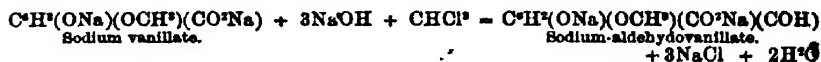
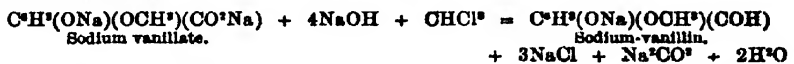
Methyl ethyl protocatechuic acid, $\text{C}^6\text{H}_3(\text{OCH}^3)(\text{OCH}^2\text{H})\text{CO}^2\text{H}$, also called ethomethoxybenzoic acid, is formed by oxidation of ethyl-eugenol, $\text{C}^6\text{H}_3(\text{OCH}^3)(\text{OCH}^2\text{H})\text{C}^6\text{H}_5$, with ordinary chromic acid mixture, or better, by treating a solution of ethyl-eugenol in glacial acetic acid with potassium dichromate. It crystallises in colourless needles, easily soluble in ether, alcohol, and solutions of caustic alkalis or alkaline carbonates; melts at 190° . Heated to 120° – 130° in a sealed tube with hydriodic acid, it yields ethyl and methyl iodides, together with protocatechuic acid:



(Wassermann, *Liebig's Annalen*, cxxxix. 306).

Metheneprotocatechuic acid, $\text{CH}_2\langle\text{O}\rangle\text{C}^6\text{H}_3\text{—CO}^2\text{H}$, produced by heating protocatechuic acid with methene iodide and potassium hydrate, is identical with piperonylic acid, which is formed, together with its aldehyde, piperonal, by oxidation of piperic acid. Ethene-protocatechuic acid is obtained in like manner by heating protocatechuic acid with potash and ethene bromide (2nd Suppl. 982, 1024).

Aldehydovanillic acid, $\text{C}^6\text{H}^4\text{O}^4 = \text{C}^6\text{H}_3(\text{OH})(\text{OCH}^3)(\text{CO}^2\text{H})(\text{COH})$ (Tiemann a. Mendelsohn, *Deut. Chem. Ges. Ber.* x. 1278).—This acid is formed, together with vanillin (methylprotocatechuic aldehyde), by the action of chloroform and a caustic alkali on vanillic acid:

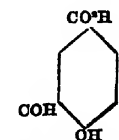


Vanillic acid (1 mol.) is boiled for five or six hours, in a flask fitted with a reflux condenser, with sodium hydrate (5 mols.) dissolved in twice its weight of water, and chloroform (1 mol.); the product is dissolved in 5–8 parts of water, and the solution is strongly acidulated with sulphuric acid, whereby a sparingly soluble compound is precipitated, which, after standing for a few hours, may be separated by filtration. The filtered solution contains vanillin, which may be separated by combination with acid sodium sulphite; and the sparingly soluble substance contains the aldehydovanillic acid, which may also be extracted by ether, and separated from the ethereal solution by agitation with an aqueous solution of acid sodium sulphite.

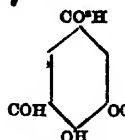
From the solution thus obtained the aldehydovanillic acid may be extracted by ether after the acid sodium sulphite has been decomposed by sulphuric acid; and on distilling off the ether, the aldehydo-acid remains as a hard yellow crystalline mass which, after several recrystallisations from boiling water, may be obtained in slender needles, having a faint yellow colour and silky lustre, and melting at 221° – 222° (uncorr.) It dissolves easily in alcohol and ether, very sparingly in cold, somewhat more readily in boiling water. It decomposes sodium carbonate with effervescence, and unites with acid sodium sulphite, exhibiting therefore the properties both of an acid and of an aldehyde.

as vanillic acid is a derivative of paraoxybenzoic acid, in which the OH-group still occupies the para-position with respect to the carboxyl, it may be expected that the

action of chloroform and NaOH on this acid will give rise to an aldehyde-derivative, in which the COH-group is likewise contiguous to the OH² thus—



Aldehydoparaoxy-
benzoic acid



Aldehydo-
vanillic acid
1 : 3 : 4 : 5

In accordance with this view it is found that aldehydovanillic acid dissolves in soda-lay with a deep yellow colour, and its aqueous solution gives a distinct reddish-violet coloration with ferric chloride, both which reactions are likewise exhibited by salicylic aldehyde.

Aldehydodimethylprotocatechuic acid,



This is the composition of opianic acid, which is produced, together with hemipinic (dimethyl-phthalic) acid, by oxidation of narcotine with MnO^2 and dilute sulphuric acid, or with nitric acid. The dimethylated acid formed by direct substitution of methyl in aldehydovanillic acid has, however, not yet been obtained; and it would probably be isomeric, not identical with opianic acid, inasmuch as it would yield, by separation of CO^2H , a methyl-vanillin having the constitution $\text{COH} : \text{OCH}^3 : \text{OCH}^3 = 1 : 2 : 3$, whereas it appears from the observations of Beckett a. Wright (*Chem. Soc. Jour.* 1876, i. 281) that opianic acid, when decomposed by distillation, yields a methyl-vanillin having the constitution $\text{COH} : \text{OCH}^3 : \text{OCH}^3 = 1 : 3 : 4$, analogous to protocatechuic acid (Tiemann a. Mendelssohn).

Trioxybenzoic Acid, $\text{C}^6\text{H}^2(\text{OH})^3\text{CO}^2\text{H}$. The only known modification of this acid is gallic acid, which may be produced artificially, by substitution of OH for Br, from the monobrominated derivative either of dioxybenzoic acid, $\text{CO}^2\text{H} : \text{OH} : \text{OH} = 1 : 2 : 4$ (p. 289), or of protocatechuic acid 1 : 3 : 4 (Barth a. Senhofer, *Deut. Chem. Ges. Ber.* viii. 1484). The position of the bromine-atom in these two dioxy-acids is not exactly known, but each of them may give rise to three monobromoderivatives, from which, by substitution of OH for Br (fusion with KHO), the following trioxybenzoic acids may be formed:

From 1 : 2 : 4 dioxybenzoic acid

$\text{CO}^2\text{H} : \text{OH} : \text{OH} : \text{OH}$				
1	2	3	4	
1	2	4	5	
1	2	4	6	

From 1 : 3 : 4 dioxybenzoic acid :

$\text{CO}^2\text{H} : \text{OH} : \text{OH} : \text{OH}$				
1	2	3	4	
1	3	4	5	
1	3	4	6	
or 1	2	4	5	

The only forms common to both these series are 1 : 2 : 3 : 4 and 1 : 2 : 4 : 5, one of which must therefore represent the constitution of gallic acid; and this inference is corroborated by the fact that gallic acid may also be formed either from di-iodosalicylic or from di-iodoparaoxybenzoic acid (Barth a. Senhofer, *loc. cit.*); but at present we have no means of determining by which of the two formulae its constitution is actually represented, but the 1 : 2 : 4 : 5 is the more probable.

When a solution of gallic acid in glycerin is diluted with an equal volume of water, the gallic acid crystallises out after some time (S. Gale, *Pharm. J. Trans.* [3], iv. 441).

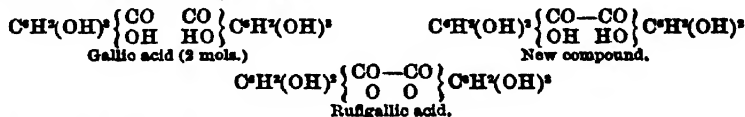
A solution of gallic acid mixed with slightly alkaline potassium or sodium *arsenite*, absorbs oxygen from the air, and acquires a deep green colour (perceptible in solutions diluted to 1 in 20,000). Dilute acids change the colour to purple-red; concentrated acids to pale yellow; alkalis reconvert the former tint, but not the latter, into green. Oxidising agents, for the most part, turn the liquid brown; reducing agents decolorise it. Gallotannic acid does not give this reaction; the presence of pyrogallie acid prevents it (Procter, *Chem. Soc. Jour.* [2], xii. 609).

Gallic acid heated to 100° with excess of bromine, is converted, with evolution of carbon dioxide, into tripromopyrogallol. Tannin heated with commercial undried bromine also yields tripromopyrogallol, a result which corroborates Schiff's view (*2nd Suppl.* 1143) that tannin is an anhydride of digallic acid (Stenhouse, *Liebig's Annalen*, clxxvii. 189).

Gallie acid treated in aqueous solution with potassium chlorate and hydrochloric acid, is converted, with violent evolution of carbon dioxide, into isotrichloroglyceric acid, $C^3H^3Cl^3O^4$ (Schredar; *Liebig's Annalen*, clixvii. 282); see GLYCERIC ACID.

Condensation-product of Gallie acid.—A saturated solution of gallie acid in cold water acidified with sulphuric acid and treated with crystallised potassium permanganate, yields a body having the composition $C^{14}H^{10}O^8$. This compound is yellow and crystalline, dissolves very sparingly in water (which, however, it colours distinctly yellow), and is easily soluble in alcohol and ether. It may be heated to 180° without alteration; when strongly heated it carbonises, giving a slight sublimate of yellow needles. Dilute sulphuric acid does not affect it on boiling, but the strong acid dissolves it, forming a solution from which it is thrown down, apparently unaltered, by water. Potash added to water in which the substance is suspended dissolves it instantly, with fine green colour, changing rapidly to blue, and ultimately to yellow. The potassium compound, formed by adding potassium acetate to the alcoholic solution, is a red-brown, gelatinous precipitate; after washing with alcohol and drying under the air-pump, it dissolves in water, forming a yellow solution, which is not affected by agitation with air, but on adding a drop of dilute potash-solution, the colour changes to green, blue, and yellow, as before.

The compound $C^{14}H^{10}O^8$ may be regarded as a condensation-product of gallie acid containing 2 atoms of hydroxyl less than 2 mols. of gallie acid, and 2 atoms of hydrogen more than rufgallie acid:



(Oser u. Flögl, *Wien Akad. Ber.* [2 Abth.] lxxii. 165).

Sulphobenzoic Acid, $C^6H^4SO^2 = C^6H^4 \left\{ \begin{array}{c} CO^2H \\ SO^2H \end{array} \right\}$ (Remsen, *Liebig's Annalen*, clxxviii. 275).—Ordinary sulphobenzoic acid, prepared by treating benzoic acid with sulphuric anhydride, has been previously shown by Remsen to be a mixture of the meta- and para-modifications, inasmuch as when fused with potash it yields a mixture of meta- and paraoxybenzoic acids (2nd Suppl. 1113). Further experiments by the same chemist have shown the proportions of the two sulpho-acids to vary considerably in different preparations, the meta-modification however generally predominating. The circumstances which determine the formation of one or the other have not been very distinctly made out; the temperature of the reaction does not appear to have much influence on the result. In one experiment in which the semi-fluid mass obtained by the action of sulphuric anhydride on benzoic acid was gently heated with a little fuming sulphuric acid till the whole was dissolved, the product was found to consist chiefly of para-sulphobenzoic acid, as on fusion with potassium hydrate it yielded a salt which crystallised from water in well-defined crystals having the form and composition of potassium paraoxybenzoate. Now the potassium salt of pure metasulphobenzoic acid is not converted into parasulphobenzoate by fusion with potassium hydrate, the sole product of this reaction being metaxybenzoic acid; consequently the parasulphobenzoic acid must have been formed directly, together with the meta-acid, by the action of fuming sulphuric acid on benzoic acid.

When the para-modification is present in considerable proportion, the separation of the two sulphobenzoic acids may be partially effected by conversion into barium salts. The acid liquid is neutralised with barium carbonate, and the excess of barium removed by sulphuric acid. The clear filtered solution is then divided into two equal parts, the barium of the one portion exactly precipitated with sulphuric acid, and the two clear solutions mixed and evaporated to the crystallising point. The liquid on cooling deposits long, flat, needle-shaped crystals of acid barium parasulphobenzoate, $(C^6H^4SO^2)_2Ba + 3H^2O$, and the mother-liquor when further evaporated yields an additional quantity of these crystals, together with prisms, apparently monoclinic, of the metasulphobenzoate. When, however, the proportion of parasulphobenzoic acid in the original product is but small, the separation cannot be effected in this way (Remsen, *Liebig's Annalen*, clxxviii. 275).

Parasulphobenzoic Acid, $C^6CO^2H.H.H.SO^2H.H.H$ (Remsen, *loc. cit.*)—This acid may be prepared by oxidation of paratoluenesulphonic acid. 26 grams of toluene are dissolved without external heating in 200 grams of fuming sulphuric acid; the solution after cooling is mixed with 2 volumes of water, and the height of the liquid in

the vessel is noted; more water is then added, and the whole distilled till the liquid is reduced to its original volume; by this means the unattacked toluene is separated from the solution of the sulpho-acid or acids. The solution is then left to cool, and 160 grams of coarsely pounded potassium dichromate are gradually added, the flask being heated in a water-bath till a brisk frothing is set up, and then removed.

When the evolution of carbonic anhydride ceases, indicating that the reaction is complete, the solution is diluted with a large quantity of water and neutralised with chalk, whereby the chromic oxide formed in the reaction, and the sulphuric acid, are precipitated, while the potassium salts of the sulpho-acid or acids remain in solution together with a little neutral potassium chromate. The chromic acid is next precipitated by the requisite quantity of baryta-water, the filtered liquid evaporated nearly to dryness, the remaining white mass neutralised with sulphuric acid, and a further quantity of that acid added just sufficient to set the sulphobenzoic acid free. Moderately strong alcohol is then added to precipitate the potassium sulphate, the solution being several times evaporated and the residue washed with alcohol till the whole of that salt is removed, and finally the alcoholic solution is boiled and evaporated over the water-bath. The sulpho-acid thus obtained is dissolved in water, and the solution divided into two equal parts, one of which is neutralised with barium carbonate, whereby, after filtration and evaporation, the acid barium salt of parasulphobenzoic acid is obtained in its characteristic form.

The crude toluenesulphonic acid used for the preparation above described contained ortho- as well as para-toluenesulphonic acid; but the product of its oxidation was not found to contain any orthosulphobenzoic acid.

Parasulphobenzoic acid, separated from the barium salt by exact precipitation with sulphuric acid and evaporation of the filtrate, is very easily soluble in water, and crystallises from very strong solutions in colourless, transparent, non-deliquescent needles (the meta-acid is deliquescent). It melts at 200° , but begins to decompose before the melting point is attained.

Potassium parasulphobenzoate, obtained from the barium salt by precipitation with potassium carbonate, is extremely soluble in water, but ultimately crystallises in well-defined transparent needles. The acid sodium salt, $C^6H^4\{SO^2Na\}CO_2H + 2\frac{1}{2}H^2O$, obtained by precipitating the barium salt with sodium carbonate, and addition of hydrochloric acid to the filtered solution, forms stellate groups of long colourless shining prisms. It is moderately soluble in cold, more easily in hot water. The corresponding meta-salt is less soluble, and crystallises in laminae. The para-salt does not give off its water of crystallisation below 310° . All the other parasulphobenzoates, and likewise the meta-salts, exhibit the same property, though not in the same degree.

The neutral barium salt, $C^6H^4\{SO^2Ba\} + 2H^2O$, obtained by neutralising the acid salt with barium carbonate, is moderately soluble in cold, very easily in hot water, and crystallises in nodular groups of small needles. The corresponding meta-salt is easily soluble, but is said not to contain water of crystallisation. The acid barium salt, $(C^6H^4SO_2)^2Ba + 3H^2O$, prepared as above described, is very sparingly soluble in cold water, and less soluble in hot water than the meta-salt. Like the latter it does not give up the whole of its water below 200° , and may be heated to a much higher temperature without decomposing. The calcium salt is an amorphous powder, more soluble in cold than in hot water, and therefore precipitated when its concentrated solution is boiled.

When the potassium salt of parasulphobenzoic acid is heated with sodium formate, terephthalic acid is produced, together with small quantities of benzoic acid, and apparently also thiohydrobenzoic acid, but not a trace of phthalic or isophthalic acid (Remsen, *loc. cit.*)

Nitroparasulphobenzoic acid, $C^6H^4(NO_2)\{SO^2H\}CO_2H$, is formed by the action of a mixture of fuming nitric and sulphuric acids on parasulphobenzoic acid (*infra*) at the boiling heat. The solution, freed from nitric acid by evaporation, then diluted with water and neutralised with barium carbonate, yields a salt which crystallises in concentric groups of long, shining, golden-yellow needles, moderately soluble in hot, less soluble in cold, water, and having the composition of neutral barium nitroparasulphobenzoate, $C^6H^4(NO_2)\{SO^2O\}CO_2O > Ba + 1\frac{1}{2}H^2O$.

The corresponding salt of nitrometasulphobenzoic acid (v. 487) is easily soluble, and crystallises with $1\frac{1}{2}$ and 3 mols. water.

Parasulphobenzoamic acid, $C^6H^4NSO^2 = C^6H^4\{SO^2NH^2\}COOH$ (Remsen, *loc. cit.*)—

This acid is formed by oxidation of paratoluenesulphamide, $C^6H^4\{SO^2NH^2\}OH$. Seven

grams of the amide are added to a mixture of 20 grams of potassium dichromate and 30 grams of strong sulphuric acid diluted with 3 vols. water, and left to cool, and the liquid is heated over a small gas flame till the product of the oxidation has completely separated; the liquid after cooling is filtered, and the solid product washed with cold water. The sulphobenzamic acid is thus obtained in fine crystals, which may be completely purified by once recrystallising them from water.

Parasulphobenzamic acid is nearly insoluble in cold, only slightly soluble in hot water, and crystallises from the aqueous solution in flat, highly lustrous prisms, sometimes more than an inch long. It dissolves easily in alcohol, and separates from the solution in smaller crystals. From the alcoholic solution, either hot or cold, it is precipitated by water in the crystalline state. It melts at a very high temperature, but decomposes before the melting point is attained (Remsen, *Liebig's Annalen*, cxxxviii. 299).

Metasulphobenzamic acid, $C^6H^4SO^2H.H.SO^2NH^2.H^2$, obtained by heating sulphobenzamide or ammonium sulphobenzozate with potash, crystallises in needles or rhombohedrons melting at 200° (v. 485).

Ammonium parasulphobenzamate, $C^6H^4\left\{SO^2NH^2\right\}CO.ONH^4$ obtained by dissolving the acid in ammonia, crystallises in needles or long laminæ, very soluble in water, and easily forming supersaturated solutions which solidify on agitation, &c. The metasulphobenzamate crystallises in laminæ.

Barium parasulphobenzamate, $(C^6H^4SO^2N)^2Ba + H^2O$, prepared by boiling the acid with barium carbonate, forms spherical groups of crystals very soluble in water.

Ethyl parasulphobenzamate, $C^6H^4\left\{SO^2NH^2\right\}CO.C^2H^5$ is produced by passing dry hydrogen chloride into a solution of the acid in absolute alcohol, and gently heating the solution on the water-bath. From this solution, evaporated to a syrupy consistence, it separates on cooling in very slender needles. In water and in ether it is less soluble than in alcohol, and in cold less than in hot water. When boiled with water it melts under the liquid before dissolving. From the hot aqueous solution it separates on cooling in parallel groups of needles having a silky lustre and sometimes two or three inches long. The melting point exhibits a remarkable anomaly. The crystals melt at 110° – 111° , but if the fused mass be then left to solidify by cooling, it melts immediately afterwards at 94° – 95° , the melting point, however, continually rising as the solid mass is left longer after the first fusion, till in about two hours it returns to the original temperature, 110° – 111° (Remsen).

Ethyl-metasulphobenzamate (v. 486) crystallises in monoclinic prisms.

SULPHOBROMOBENZOIC ACIDS, $C^6H^3Br(SO^2H)(CO^2H)$.—The sulphometabromobenzoic acid which Roeters van Lennep obtained by heating bromobenzoic acid with sulphuric anhydride (2nd Suppl. 1114), is converted by sodium-amalgam into a sulphobenzoic acid, the constitution of which has not yet been determined. By fusion with potash it yields a dioxymbenzoic acid; and when fused with sodium formate, a very small quantity of trimesic acid (Böttinger, *Dout. Chem. Ges. Ber.* vii. 1778).

Sulphoparabromobenzoic Acid.—When vapour of sulphuric anhydride is passed into parabromobenzoic acid, and the resulting liquid is heated for a day to 160° , the whole is converted into a mixture of two sulpho-acids, one yielding a very soluble, the other a sparingly soluble barium salt. The acid separated from the first of these (β -sulphoparabromobenzoic acid) is identical with that which Weiss obtained (*Jahresb. f. Chem.* 1873, 658) by oxidation of β -parabromotoluenesulphonic acid, $C^6H^3Br.SO^2H.H.Br.H^2$, with chromic acid. It is a very soluble crystalline mass. Its barium salt, $C^6H^3Br.SO^2O.H.Br.H.H$, forms small, very soluble microscopic

[Ba.]

four-sided plates. The neutral calcium salt, likewise anhydrous, forms extremely soluble microscopic laminæ. The lead, potassium, and sodium salts are also extremely soluble (Weiss).

The less soluble barium salt obtained by Böttinger, which constitutes the chief part of the product, crystallises in large hard groups of transparent crystals containing 3 mols. water, 1 mol. of which is given off at 220° . The acid barium salt is also very slightly soluble, and crystallises in needles containing 2 mols. water. The copper salt crystallises in broad, blue, extremely soluble needles, containing $3H^2O$. The free acid is obtained, by evaporation over the water-bath and in the exsiccator, in long thin transparent prisms (Böttinger). This acid should be identical with that which Hässelbarth obtained (*Jahresb.* 1873, 656) by oxidation of α -parabromotoluenesulphonic acid, $C^6H^3.H.SO^2H.Br.H.H$, since parabromobenzoic acid, $C^6H^3Br.H.H.Br.H^2$, can yield only two sulphonic acids, viz. those in which the

radicles CO^2H , SO^2H , and Br are respectively in the positions 1 : 2 : 4 and 1 : 3 : 4, and, in fact, the only difference observed between the acids described by Hässelbarth and by Böttinger is that the barium salt of the former crystallises with 3 mols., that of the latter with $1\frac{1}{2}$ mol. water. The neutral calcium salt of Hässelbarth's acid is anhydrous, more soluble than the other salts, and crystallises in small needles, which under the microscope appear as four-sided pointed prisms. The neutral lead salt, $\text{C}^6\text{H}^3\text{Br}.\text{SO}^2.\text{Pb}.\text{CO}^2 + 2\text{H}^2\text{O}$, forms groups of small needles. The acid potassium salt, $\text{C}^6\text{H}^3\text{Br}.\text{CO}^2\text{H}.\text{SO}^2\text{K}$, crystallises in long slender colourless needles.

Sulphorthobromobenzoic acid, $\text{C}^6\text{H}^3.\text{CO}^2\text{H}.\text{Br}.\text{SO}^2\text{H}^2$, or $\text{C}^6\text{H}^3.\text{CO}^2\text{H}.\text{Br}.\text{H}.\text{H}.\text{SO}^2\text{H}.\text{H}$, is obtained by oxidation of orthobromotoluenesulphonic acid with chromic acid mixture, whereby, however, a considerable portion of the bromotoluenesulphonic acid is burnt to carbon dioxide and acetic acid.

Acid potassium sulphorthobromobenzoate, $\text{C}^6\text{H}^3\text{Br}.\text{SO}^2\text{K}.\text{CO}^2\text{H} + 1\frac{1}{2}\text{H}^2\text{O}$, crystallises in large thin laminæ resembling naphthalene, which traverse the liquid in fan-shaped groups, and are very soluble in water. The neutral barium salt, $\text{C}^6\text{H}^3\text{Br}.\text{SO}^2.\text{CO}^2\text{Ba} + 2\text{H}^2\text{O}$, separates from its syrupy aqueous solution, after several weeks, in indistinct deliquescent scales. By mixing its aqueous solution with a quantity of strong alcohol sufficient to produce a permanent precipitate, and covering the liquid with a layer of alcohol, the salt is obtained in tufts of long, slender, shining, colourless needles, which are extremely soluble in water and in alcohol, and give off part of their crystallisation-water over sulphuric acid. The neutral calcium salt, which is also extremely soluble, forms long needles having a silky lustre. The neutral lead salt, $\text{C}^6\text{H}^3\text{Br}.\text{SO}^2.\text{CO}^2\text{Pb} + 2\text{H}^2\text{O}$, crystallises in small, delicate, white, shining needles (Hübner a. Retschy, *Zeitschr. f. Chem.* 1871, 629).

Sulphoparachlorobenzoic Acid, $\text{C}^6\text{H}^4\text{Cl}(\text{SO}^2\text{H}).\text{CO}^2\text{H}(\text{CO}^2\text{H} : \text{Cl} = 1 : 4)$, is prepared by passing the vapour of sulphuric anhydride into parachlorobenzoic acid dried at 100° , and finely triturated; or by mixing parachlorobenzoic acid with fuming sulphuric acid at the ordinary temperature, and promoting the reaction by gently warming the mixture. Its formation is accompanied by that of a small quantity of an isomeric acid, from which it may be separated by crystallisation of the lead salts.

Sulphoparachlorobenzoic acid crystallises from its aqueous solution in white needles containing 3 mols. of water. When heated it yields a sublimate of parachlorobenzoic acid. The lead salt crystallises in rhombic tables, with 4 mols. of water; its hot aqueous solution readily deposits a basic salt. The barium salt forms tabular crystals with 3 mols. of water. The copper salt is deposited in long blue needles, containing 6 mols. of water and deliquescing in the air. The neutral potassium salt crystallises in needles (Th. Cöllen, *Deut. Chem. Ges. Ber.* ix. 758).

Disulphobenzoic Acid, $\text{C}^6\text{H}^4(\text{SO}^2\text{H})^2(\text{CO}^2\text{H})$. Barth a. Senhofer (*Liebig's Annalen*, clix. 217) prepare an acid of this composition by heating 10 grams of benzoic acid with 20 of strong sulphuric acid, adding, after cooling, 15 of phosphoric anhydride and 15–20 of a mixture of sulphuric anhydride and strong sulphuric acid, and heating the mixture for three or four hours in strong glass tubes. The aqueous solution of the brown thick liquid thus obtained is neutralised with barium carbonate, and the filtered and concentrated solution is mixed with hydrochloric acid, whereupon the acid barium salt, $\text{C}^6\text{H}^4(\text{CO}^2\text{H}).(\text{SO}^2)^2\text{Ba} + 2\text{H}^2\text{O}$, separates in tufts of microscopic needles, which are anhydrous when dried at 160° . The neutral barium salt, $(\text{C}^6\text{H}^4\text{SO}^2)^2\text{Ba} + 7\text{H}^2\text{O}$, obtained by boiling the solution of the acid salt with barium carbonate, crystallises in small well-defined prisms, which give off their water at 160° . The copper salt, $(\text{C}^6\text{H}^4\text{SO}^2)^2\text{Cu} + 8\frac{1}{2}\text{H}^2\text{O}$, is a light green crystalline mass made up of slender microscopic needles; gives off its water at 130° . The silver salt, $\text{C}^6\text{H}^4\text{SO}^2\text{O}^-\text{Ag}^+ + 2\text{H}^2\text{O}$, is a white crystalline precipitate which blackens but slowly on exposure to light; anhydrous at 130° . The cadmium salt is a white crystalline very soluble mass. The sodium salt forms large, thick, well-defined prisms very soluble in water. The potassium salt, $\text{C}^6\text{H}^4\text{SO}^2\text{O}^-\text{K}^+ + 1\frac{1}{2}\text{H}^2\text{O}$, forms soft slender needles, which give off their water at 130° . The free acid is best prepared by treating the neutral barium salt with as nearly as possible the exact quantity of sulphuric acid required to decompose it, evaporating the solution to dryness, dissolving the residue, in case it still contains barium, in absolute alcohol, distilling off the alcohol, redissolving the residue in water, and leaving the solution to evaporate in a vacuum over sulphuric acid. As thus obtained, it forms a white, crystalline, extremely hygroscopic mass, consisting of microscopic needle-shaped prisms. It often separates in smooth needles an inch long when the contents of the tubes in which it is prepared are mixed with a little water, and left for some time in an open vessel. The amount of water in the acid crystallised at ordinary temperatures has not been determined. When

dried at 130°, at which temperature it already begins to turn brown, it has the composition $C^6H^4(CO^2H)(SO^2H)^2 + H^2O$. When heated to 140° it turns quite brown, and appears to give off its water of crystallisation.

By fusion with potash, this acid is converted into a dioxybenzoic acid, $C^6H^4(OH)^2.CO^2H$, which melts at 220°, and is not coloured by ferric chloride.

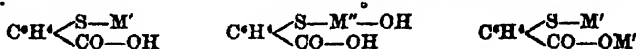
Another disulphobenzoic acid is obtained by oxidation of α -toluenedisulphonic acid with chromic acid mixture. Its potassium salt, $C^6H^4(SO^2K)(CO^2K) + 2H^2O$, forms large brittle easily soluble prisms. The acid potassium salt, $C^6H^4SO^2K.CO^2K + H^2O$, is distinguished by its great facility of crystallisation, and sparing solubility. The barium salt forms indistinctly crystalline granular masses.

By fusion with potash, this acid yields a dioxybenzoic acid apparently identical with that which Ascher obtained from para-nitrotoluene (2nd Suppl. 432), melting in the crystallised state at 148°, in the dehydrated state at 194°, and coloured dark rose-red by ferric chloride. This dioxybenzoic acid—and, therefore, the disulphobenzoic acid from which it is prepared—has the constitution 1 : 2 : 4 (CO^2H in 1) (P. Hakanson, *Deut. Chem. Ges. Ber.* v. 1088).

Thiobenzoic Acid, $C^6H^4O^2S = C^6H^4 \begin{Bmatrix} SH \\ COOH \end{Bmatrix}$. This acid, the sulphur analogue of oxybenzoic acid, was discovered by Hübner a. Upmann, who prepared it by the action of nascent hydrogen on sulphobenzoic chloride, $C^6H^4.OOOSH.SO^2Cl$ (2nd Suppl. 1155). The product which they obtained appears, however, to have been a mixture of thio- and dithiobenzoic acids; and, moreover, it is by no means certain that the sulphobenzoic acid from which it was derived consisted of one modification only. The investigation has therefore been continued by Frerichs (*Deut. Chem. Ges. Ber.* vii. 792) with thiobenzoic acid prepared from sulphobenzoic chloride obtained by decomposition of well-crystallised sodium metasulphobenzoate.

The acid, purified by volatilisation in a stream of carbonic anhydride, forms delicate colourless laminae melting at 146°–147°. When dry it volatilises in the air without decomposition. It is moderately soluble in water, more freely in alcohol.

The metallic thiobenzoates were mostly prepared by double decomposition from the ammonium salt. From their sparing solubility, the colour of some of them, and the circumstance that sulphur in its compounds often exhibits greater affinity for the metal than oxygen does, it is inferred that the metal in the thiobenzoates is directly combined with the sulphur, their composition being accordingly represented by the formulæ:



The silver salt, $AgS.C^6H^4.COOH$, is a lemon-yellow precipitate, formed of well-defined microscopic crystals.

The copper salt, $C^6H^4 \begin{Bmatrix} S.Cu.OH \\ CO.OH \end{Bmatrix}$, is a green precipitate, made up of well-defined

~~microscopic crystals.~~ $C^6H^4 \begin{Bmatrix} S.Pb.OH \\ COOH \end{Bmatrix} + 2H^2O$, or $C^6H^4 \begin{Bmatrix} S \\ COO \end{Bmatrix} Pb + 3H^2O$, may be formed directly, as a lemon-yellow precipitate, by adding lead acetate to an aqueous or alcoholic solution of thiobenzoic acid.

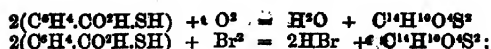
The mercuric salt, $Hg \begin{Bmatrix} S-C^6H^4-COOH \\ S-C^6H^4-COOH \end{Bmatrix}$, is formed by dissolving mercuric oxide in the free acid, and separates from the solution in colourless capillary needles.

The barium salt, $Ba \begin{Bmatrix} S-C^6H^4-COOH \\ S-C^6H^4-COOH \end{Bmatrix} + 2\frac{1}{2}H^2O$, is a nearly white precipitate.

Bromothiobenzoic acid, $C^6H^4Br \begin{Bmatrix} SH \\ COOH \end{Bmatrix}$, formed by the action of tin and hydrochloric acid on liquid bromosulphobenzoic chloride, crystallises in thin colourless plates, somewhat sparingly soluble in cold water, not so easily altered by exposure to moist air as thiobenzoic acid. It volatilises without decomposition, and melts at 192°–194°. The lead salt, $C^6H^4Br \begin{Bmatrix} S-Pb-OH \\ CO-OH \end{Bmatrix} + 2H^2O$, or $C^6H^4Br \begin{Bmatrix} S \\ COO \end{Bmatrix} Pb + 3H^2O$, separates on adding lead acetate to the ammonium salt, as a lemon-yellow, insoluble, crystalline precipitate (Frerichs).

Dithiobenzoic Acid, $C^6H^4O^2S^2 = C^6H^4 \begin{Bmatrix} COOHS \\ COOHS \end{Bmatrix}$ (Hübner, *loc. cit.*) This acid,

originally obtained by Hübner a. Upmann, is easily formed from thiobenzoic acid by exposure to the air in the moist state, or more quickly by treating the aqueous solution with bromine-water:



also, according to Griess (*J. pr. Chem.* cix. 102), by decomposing the aurochloride of diathobenzoic acid with hydrogen sulphide.

Dithiobenzoic acid is nearly insoluble in water, very slightly soluble in alcohol, and crystallises in microscopic needles melting at 242° – 244° .

The metallic dithiobenzoates, obtained by double decomposition from the ammonium salt, exhibit no resemblance whatever to the metallic derivatives of the thiophenols. The *barium salt*, $(\text{C}^6\text{H}^4\text{SCOO}^2)^2\text{Ba} + 3\text{H}^2\text{O}$, is a white precipitate insoluble in water, and giving off $\frac{1}{2}$ mol. H^2O when left for a long time over oil of vitriol. The *bepper salt*, $[\text{C}^6\text{H}^4\text{SCOO}(\text{CuOH})]^2 + 5\text{H}^2\text{O}$, is a light blue non-crystalline precipitate, insoluble in water. The *lead salt*, $(\text{C}^6\text{H}^4\text{S.COO}^2)^2\text{Pb} + \text{H}^2\text{O}$, is a white precipitate insoluble in water. The *silver salt*, $\text{C}^6\text{H}^4\text{S.COO}^2\text{Ag} + \frac{1}{2}\text{H}^2\text{O}$, is a yellowish-white precipitate insoluble in water. This salt and the mercuric salt are not produced by treating the respective oxides with free dithiobenzoic acid. A solution of ammonium dithiobenzoate mixed with mercuric chloride gives a yellowish-white precipitate, apparently consisting of the mercury salt mixed with mercurous chloride.

The following table gives a comparative view of the structure and principal properties of the derivatives of benzoic acid:—

Abbreviated symbol of compound	Physical properties	Positions of the substituted radicals (CO ² H in 1)				
		Ortho 2	Meta 3	Para 4	Meta 5	Ortho 6
Cl	Needles; m. p. 137° ; more soluble in water than the <i>o</i> - or <i>m</i> -modification.	Cl	—	—	—	—
—	Needles; m. p. 152° ; very slightly soluble in water	—	Cl	—	—	—
—	Scales; m. p. 234°	—	—	Cl	—	—
Cl.Cl	Needles; m. p. 201° ; slightly soluble in water	—	Cl	Cl	—	—
—	β . Shining needles; m. p. 156° ; b. p. 301° ; soluble in 1,200 pts. cold water; more soluble at 100°	—	Cl	—	—	Cl
—	γ . Small needles; m. p. 126.5° ; easily sublimable	Cl	—	Cl	—	—
Br	Long needles; m. p. 147° – 148° ; more soluble in water than <i>m</i> - or <i>p</i> -	Br	—	—	—	—
—	Needles; m. p. 155° ; slightly soluble in water	—	Br	—	—	—
—	Needles; m. p. 250° † nearly insoluble in water	—	—	Br	—	—
Br.Br	Small needles; m. p. 227° – 230° ; slightly soluble in water, easily in alcohol	—	Br	Br	—	—
—	Separates from water in flocks; m. p. 208° – 209° ; sublimes in flat needles	—	Br	—	Br	—
—	Melts at 151° – 152°	—	Br	—	—	Br
I	Needles; m. p. 169° ; easily sublimable	I	—	—	—	—
—	Needles; m. p. 185° – 187° ; sublimable; slightly soluble	—	I	—	—	—
—	Laminæ; m. p. 267°	—	—	I	—	—
NO ²	Prisms; m. p. 148° ; soluble in 164 pts. water at 16.5°	NO ²	—	—	—	—
—	Needles or laminæ; m. p. 141° – 142° ; soluble in 425 pts. water at 16.5°	—	NO ²	—	—	—
—	Yellowish laminæ; m. p. 240° ; less soluble than <i>m</i> -	—	—	NO ²	—	—
NO ² .NO ²	Prisms; m. p. 140° ; with Sn and HCl yields (1 : 2 : 5) diamidobenzoic acid	NO ²	—	—	NO ²	—
—	Rhombic plates or prisms; m. p. 179° . With Sn and HCl yields CO ² and (1 : 3) diamidobenzene	NO ²	—	NO ²	—	—
—	Felted needles; m. p. 202° . With Sn and HCl yields CO ² and (1 : 3) diamidobenzene	NO ²	—	—	—	NO ²

BENZOIC ACIDS (SUBSTITUTED).

Abbreviated symbol of compound	Physical properties	Positions of the substituted radicals (OO'H in 1)				
		Ortho 2	Meta 3	Para 4	Meta 5	Ortho 6
NO ² .NO ²	Crystallises from water in large square plates, from alcohol in prisms; m. p. 204°-205°. With Sn and HCl yields (1 : 8 : 5) diamidobenzoic acid	—	NO ²	—	—	—
NO ² .Br	Melts at 250°; very slightly soluble in water	NO ²	Br	—	—	—
—	Melts at 140°-141°; more soluble than 1 : 2 : 3. Both these acids are reducible to (1 : 8) amidobenzoic acid	NO ²	—	—	Br	—
NH ²	Thin prisms or laminae; m. p. 144°; easily soluble in hot water and in alcohol	NH ²	—	—	—	—
—	Needles; m. p. 178°-174°; very soluble in hot, slightly in cold water	—	NH ²	—	—	—
—	Long needles; m. p. 186°-187°; moderately soluble	—	—	NH ²	—	—
NH(C ² H ⁵)	Ethylamidobenzoic acid.—Prisms; m. p. 112°. Unites with bases and with acids	—	NH(C ² H ⁵)	—	—	—
N(C ² H ⁵) ²	Diethylamidobenzoic acid.—m. p. 90°; otherwise resembles the last	—	N(C ² H ⁵) ²	—	—	—
N(CH ³) ²	Short broad needles; m. p. 235°	—	—	N(CH ³) ²	—	—
NH(C ² H ⁵ O)	Acetylmetamidobenzoic acid.—Crystalline powder, nearly insoluble in cold water and ether; slightly soluble in boiling water, easily in boiling alcohol; melts at 220°-230°; sublimes at 200°	—	NH(C ² H ⁵ O)	—	—	—
—	Acetyl-p-amidobenzoic acid.—Needles slightly soluble in water; more easily in alcohol; m. p. about 250°	—	—	NH(C ² H ⁵ O)	—	—
NH ² .NH ²	From (1 : 2 : 5), nitramidobenzoic acid (NO ² in 2). Needles or laminae slightly soluble in cold water; resolved by distillation into CO ² and (1 : 4) diamidobenzene	NH ²	—	—	NH ²	—
—	From (1 : 2 : 3) nitramidobenzoic acid (NO ² in 2). Similar to the last; yields (1 : 2) diamidobenzene	NH ²	NH ²	—	—	—
—	From (1 : 3 : 4) nitramidobenzoic acid (NH ² in 3). Similar to the preceding; yields (1 : 2) diamidobenzene	—	NH ²	NH ²	—	—
—	From the three corresponding dinitrobenzoic acids. Resolved by distillation into CO ² and (1 : 8) diamidobenzene. The (1 : 8 : 5) acid melts at 240°	NH ² NH ²	— —	NH ² —	— —	— NH ²
NH ² .Br	From (1 : 8 : 4) nitrobromobenzoic acid. Colourless or light-yellow needles, m. p. 220°-221°	—	NH ²	Br	—	—
—	Needles slightly soluble in water; m. p. 171°-172°	NH ²	Br	—	—	—
—	Needles slightly soluble in water; m. p. 208°	NH ²	—	—	Br	—
NH ² .NO ²	Nitro-m-amidobenzoic acids.—From the three corresponding dinitro-uramidobenzoic acids by boiling with water; yellow needles	NO ² NO ²	— —	— —	NH ²	—
—	Nitro-p-amidobenzoic acid.—From dinitro-p-uramidobenzoic acid; deep yellow needles; m. p. 284°	—	NO ²	NH ²	—	—
—	Nitro-o-amidobenzoic acid.—Long needles; m. p. 205°; reduced by sodium amalgam to (1 : 2) amidobenzoic acid	NH ²	NO ²	—	—	—
—	Long needles; m. p. 270°; reduced like the last	NH ²	—	—	NO ²	—
NH ² .NO ² .NO ²	Chrysanic acid.—Golden-yellow needles, m. p. 259; nearly insoluble in cold water	—	NO ²	NH ²	NO ²	—
NH ² .NH ² .NH ²	By reduction of chrysanic acid. Shining needles with H ² O. Resolved by distillation into CO ² and (1 : 3 : 4 : 5) triamidobenzene	—	NH ²	NH ²	NH ²	—

Abbreviated symbol of compound	Physical properties	Positions of the substituted radicals (CO ² H in 1)				
		Ortho 2	Meta 3	Para 4	Meta 5	Ortho 6
OH	<i>Salicylic acid</i> .—Prisms; m. p. 155°–156°; subliming when slowly heated; decomposed by rapid heating into CO ² and phenol; very slightly soluble in cold, moderately in boiling water, easily in alcohol and ether; gives deep violet colour with ferric chloride	OH	—	—	—	—
—	<i>Oxybenzoic acid</i> .—Microscopic plates or nodules of larger crystals; m. p. 200°; distils almost undecomposed; slightly soluble in cold, more freely in hot water. No colour with ferric chloride	—	OH	—	—	—
OH	<i>Paraoxybenzoic acid</i> .—Crystallises from water in monoclinic prisms with 1H ² O; melts (anhyd.) at 210°, partly decomposing into CO ² and C ⁶ H ⁵ O; more soluble in cold water than (1 : 2); still more in hot water and in alcohol. With ferric chloride, yellow amorphous prisms soluble in excess	—	—	OH	—	—
OCH ³	Colourless plates; m. p. 98·5°; resolved at 200° into CO ² and anisol; slightly soluble in cold water, easily in hot water and in alcohol	OCH ³	—	—	—	—
OCH ³	Long needles; m. p. 106°; subliming undecomposed; slightly soluble in cold, easily in hot water and in alcohol	—	OCH ³	—	—	—
—	<i>Anisic acid</i> .—Large prisms; m. p. 175°; sublimable; nearly insoluble in cold water, easily soluble in alcohol	—	—	OCH ³	—	—
OC ² H ⁵	Radiate mass; m. p. 13·5°; resolved at 800° into CO ² and C ⁶ H ⁵ .O.C ² H ⁵	OC ² H ⁵	—	—	—	—
—	Colourless needles; m. p. 137°	—	OC ² H ⁵	—	—	—
—	Needles; m. p. 195°; sublimable; slightly soluble in boiling water	—	—	OC ² H ⁵	—	—
O.C ² H ⁵ O	Slender colourless prisms	OC ² H ⁵ O	—	—	—	—
—	Colourless crystals; m. p. 127°	—	OC ² H ⁵ O	—	—	—
OH.Cl	Colourless needles; m. p. 172·5°. Solution coloured violet by ferric chloride	OH	—	—	Cl	—
OH.Br	Colourless needles; m. p. 164°–165°; sublimes at 150°–155°. Resolved by heating with lime into CO ² and (1 : 4) bromophenol	OH	—	—	Br	—
—	Melts at 219°–220°; more soluble in water than (1 : 2 : 5)	OH	Br	—	—	—
OH.I	Produced simultaneously, together with C ⁶ H ³ (OH) ₃ .CO ² H, by the action of iodine and HgO on alcoholic salicylic acid. One melts at 184°, the other at 195°–196°	OH	—	I	—	—
OH.I.I		OH	—	—	I	—
OH.I.I	White felted mass; m. p. 220°; violet with ferric chloride. Fused with KOH yields gallic acid	OH	—	I	I	—
OH.NO ²	<i>Nitrosalicylic acid</i> (ortho).—Crystallises with 1H ² O in needles melting at 125°; dehydrated acid at 144°–145°	OH	NO ²	—	—	—
—	<i>Nitrosalicylic acid</i> (para).—Long anhydrous needles; m. p. 238°; slightly soluble in cold water; solution coloured blood-red by Fe ² Cl ⁶	OH	—	—	NO ²	—
—	<i>Nitro-p-oxybenzoic acid</i> .—Small flesh-coloured crystals	—	NO ²	OH	—	—
OCH ³ .NO ²	<i>Nitranisic acid</i> .—Shining crystals; m. p. 186°–187°. Heated with water to 220°, yields CO ² , methyl alcohol, and ortho-nitrophenol	—	NO ²	OCH ³	—	—
OH.NO ² .NO ²	<i>Dinitro-p-oxybenzoic acid</i> .—Light-yellow	—	NO ²	OH	NO ²	—

Abbreviated symbol of compound	Physical properties	Positions of the substituted radicals (CO ² H in 1)				
		Ortho 2	Meta 3	Para 4	Meta 5	Ortho 6
OCH ³ .NO ² .NO ²	or bronze rhombic plates; m. p. 285°-287° <i>Dinitranisic acid</i> .—Long shining needles, m. p. 181°-182° (Salkowski). Heated with water to 150°, it yields dinitro- <i>p</i> -oxybenzoic acid, and then <i>p</i> -dinitrophenol: C ⁶ H ³ NO ² .OH.NO ² .H ²	—	NO ²	OCH ³	NO ²	—
OH.NH ²	<i>Amidosalicylic acid</i> (ortho-).—Hydrochloride forms decomposable, easily soluble needles — (para-). Hydrochloride forms small, thick, brownish needles, easily soluble in hot water	OH	NH ²	—	—	—
—	—	OH	—	—	NH ²	—
OH.NH(C ² H ³ O)	<i>Acetyl-<i>p</i>-amidosalicylic acid</i> .—Crystallises at low temperatures with 1H ² O in thick colourless needles, very soluble in water and alcohol; m. p. 218°	OH	—	—	NH(C ² H ³ O)	—
OH.CO.H	<i>Aldehyde-salicylic acid</i> (ortho-).—Delicate needles; m. p. 166°. Calcium salt distilled with lime yields salicylic aldehyde — (para-). Delicate yellowish needles; m. p. 248°-249°. Ca-salt distilled with lime yields <i>p</i> -oxybenzoic aldehyde	OH	CO.H	—	—	—
—	<i>Aldehyde-<i>p</i>-oxybenzoic acid</i> .—Thin yellow prisms; m. p. 243°-244°. Ca-salt distilled yields salicylic aldehyde	OH	—	—	CO.H	—
—	<i>Dioxybenzoic acid</i> .—Prisms or thin needles melting with decomposition at 222°; not coloured by ferric chloride	—	CO.H	OH	—	—
OH.OH	Needles with 1½ or 2H ² O; m. p. 148°; anhyd. at 194°. Dark rose-red with ferric chloride	OH or OH	OH	—	—	OH
—	<i>Oxy-salicylic acid</i> .—Anhydrous needles or prisms; m. p. 196°-197°. Decomposed by heat into CO ² and hydroquinone. With Fe ² Cl ⁶ deep blue, changed to red by NH ³ or dilute Na ² CO ³	OH	—	—	OH	—
—	<i>Protocatechuic acid</i> .—Lamine or needles with 1H ² O; melts (anhyd.) at 199°. Decomposed at higher temperature into CO ² and pyrocatechin. With Fe ² Cl ⁶ , green, changed by dilute Na ² CO ³ to blue and red	—	OH	OH	—	—
OH.OCH ³	<i>Vanillic acid</i> .—White laminar mass; m. p. 211°-212°; sublimable; no colour with ferric chloride	—	OCH ³	OH	—	—
—	<i>Isovanillic acid</i> .—m. p. 250°	—	OH	OCH ³	—	—
OC ² H ³ O.OCH ³	<i>Acetovanillic acid</i> .—Needles; m. p. 142°	—	OCH ³	OC ² H ³ O	—	—
OCH ³ .OCH ³	<i>Veratric acid</i> .—Colourless needles; m. p. 179°-5°. Heated with lime yields CO ² and dimethyl-pyrocatechin	—	OCH ³	OCH ³	—	—
OCH ³ .OC ² H ³	<i>Ethyl-vanillic acid</i> .—Needles; m. p. 190°	—	OC ² H ³	OCH ³	—	—
OC ² H ³ .OC ² H ³	<i>Diethyl-protocatechuic acid</i> .—Needles; m. p. 149°	—	OC ² H ³	OC ² H ³	—	—
O—CH ² —O	<i>Piperonylic acid</i> .—Needles; m. p. 228°. Sublimable. Resolved by heating with HCl into protocatechuic acid and carbon	—	O—CH ² —O	—	—	—
O—C ² H ⁴ —O	<i>Ethene-protocatechuic acid</i> .—Shifting prisms; m. p. 188°-5°. Sublimable	—	O—C ² H ⁴ —O	—	—	—
OCH ³ .OH.CO.H	<i>Aldehydevanillic acid</i> .—Silky needles; m. p. 221°-222°. Red-violet with ferric chloride	—	OCH ³	HO	CO.H	—
OH.OH.OH	<i>Gallie acid</i> .—Slender silky prisms with 1 mol. H ² O. Blue-black prisms with ferric chloride. Reduces gold and silver solutions	OH	—	OH	OH	—

BENZOIC ALDEHYDE.

Abbreviated symbol of compound	Physical properties	Positions of the substituted radicals (OO ² H in 1)				
		Ortho 2	Meta 3	Para 4	Meta 5	Ortho 6
SO ³ H	<i>Sulphobenzoic acid</i> .—Crystalline, very deliquescent, strongly acid mass. Distilled with PCl ⁵ , yields <i>m</i> -chlorobenzoyl chloride. Bibasic	—	SO ³ H	—	—	—
—	Needles; very soluble, but not deliquescent; m. p. above 200°. Bibasic	—	—	SO ³ H	—	—
SO ³ H.SO ³ H	Deliquescent prisms, a. Tribasic	{ SO ³ H or SO ³ H	SO ³ H	—	—	—
SO ³ H.SO ³ H	Convertible into (1 : 2 : 4) dioxibenzoic acid	SO ³ H	—	SO ³ H	—	SO ³ H
SH	<i>Thiobenzoic acid</i> .—Laminae moderately soluble in water; m. p. 146°–147°. When dry, volatilises undecomposed in the air	—	SH	—	—	—

BENZOIC ALDEHYDE, BENZALDEHYDE, or BENZAL, C⁶H⁵.CHO. This compound is formed in small quantity, together with several other products, by heating benzyl chloride, C⁶H⁵Cl, with water (Zincke, *Deut. Chem. Ges. Ber.* vii. 146).

Solubility.—According to Flückiger (*Arch. Pharm.* [3], vii. 103), the ordinary statement that bitter almond oil dissolves in 30 parts of water is founded on an error: he finds that pure benzaldehyde (separated from its compound with acid sodium sulphite) is very slightly soluble in water, not dissolving completely even in 300 parts of water.

On the Formation of Hydrobenzoin and Isohydrobenzoin by the Action of Sodium-amalgam on Benzaldehyde in Aqueous or Alcoholic Solution, see 2nd Suppl. 171.

On the Compound of Benzaldehyde with Urethane, see URETHANES.

Chlorobenzaldehyde, C⁶H⁴($\begin{smallmatrix} \text{Cl} \\ \diagup \\ \text{CHO} \end{smallmatrix}$). The *ortho*-modification is formed by heating orthochlorobenzalchloride, C⁶H⁴Cl².Cl.H² (chlorobenzylene chloride, 1st Suppl. 281), with water to 170°, and distils over with the aqueous vapour as a colourless oil, smelling like bitter almond oil, having a sp. gr. of 1.29 at 8°, and boiling at 210°–220°. It forms a crystalline compound with acid sodium sulphite. It dissolves in fuming nitric acid, and water added to the solution throws down the compound C⁶H⁴(NO²)Cl—CHO, which crystallises from alcohol in small needles. By oxidation with chromic acid mixture, orthochlorobenzaldehyde is converted into orthochlorobenzoic acid, C⁶.CO²H.Cl.H² (L. Henry, *Deut. Chem. Ges. Ber.* ii. 135).

The *para*-modification, C⁶.CHO.H.Cl.H², is formed by passing chlorine into bitter almond oil mixed with iodine; by boiling chlorobenzyl chloride, C⁶H⁴Cl—CH²Cl, with a solution of lead nitrate; and by heating parachlorobenzal chloride, C⁶.CHCl².H.H.Cl.H², with water. It is a colourless liquid which boils without decomposition (Beilstein a. Kuhlberg, *Liebig's Annalen*, cxlvii. 339), and when exposed to the air quickly absorbs oxygen, and is converted into parachlorobenzoic acid (Berlin, *ibid.* cli. 140).

Dichlorobenzaldehyde, C⁶H²Cl².CHO, is formed by heating dichlorobenzal chloride, C⁶H²Cl⁴.CHCl² (1st Suppl. 282), with water to 200°. The product is washed with weak ammonia, and agitated with a strong solution of acid potassium sulphite; and the resulting double salt is washed with cold water and decomposed with soda-solution. The aldehyde crystallises in slender needles, and volatilises with aqueous vapour. Its vapours attack the eyes. It dissolves in alcohol and in a large quantity of hot water. On exposure to the air it is converted into dichlorobenzoic acid melting at 128° (1 : 2 : 4), see p. 265. *Hydrogen sulphide*, passed into its alcoholic solution forms an amorphous precipitate (Beilstein a. Kuhlberg, *Liebig's Annalen*, clii. 424).

Trichlorobenzaldehyde, C⁶H²Cl³.CHO, is formed by heating the chloride CHCl³.CHCl² (1st Suppl. 283) with water to 260°, and purified in the manner above described. It crystallises in white slender needles melting at 110°–111°, easily soluble in alcohol, insoluble in water even at the boiling heat; has a pungent odour; reacts with hydrogen sulphide like the preceding compound (Beilstein a. Kuhlberg, *loc. cit.*)

Nitrobenzaldehyde, C⁶H⁴(NO²).CHO. Of the three possible modifications of this compound, one, viz., the *meta*, has long been known. It is obtained by the

action of a mixture of nitric and sulphuric acids on bitter almond oil; crystallises in colourless shining needles melting at 58° , and is converted by oxidising agents into metanitrobenzoic acid (i. 570).

Another modification has lately been described by Fittica (*Deut. Chem. Ges. Ber.* x. 1630). It is obtained, together with the preceding, by cautiously dropping a mixture of equal weights of benzaldehyde and ethyl nitrate into a quantity of strong sulphuric acid equal to about four times the volume of the mixture, till the temperature of the liquid rises to 30° , then cooling it, and continuing the dropping at such a rate as to maintain a uniform temperature of 30° – 35° . When the action is over, the mixture is to be set aside and frequently agitated—care being taken that the temperature does not rise above 40° —till a sample poured into water no longer emits any odour of bitter almond oil. The whole is then poured into water, the oil which settles down is washed successively with water, solution of sodium carbonate, and again with water, and the half solid mass is left to itself for some days. By this treatment the crystalline portion (ordinary nitrobenzaldehyde) is separated from a light-brown oil, which may be obtained by pressing the mass between glass plates.

This oily liquid exhibits the composition of nitrobenzaldehyde. It has an odour somewhat like that of bitter almond oil, reduces an alcoholic ammoniacal silver solution, and dissolves in a concentrated solution of acid sodium sulphite, but does not form therewith a crystalline compound. It may be distilled, though not quite without decomposition, under a pressure of 50 mm. The distillate is at first light yellow, but very quickly turns brown, a change which is not exhibited by the undistilled aldehyde.

By oxidation with chromic acid in glacial acetic acid solution, this nitrobenzaldehyde is converted into a nitrobenzoic acid melting at 127° . This is Fittica's fourth nitrobenzoic acid, and he regards its formation in this manner as a decisive proof of its separate identity. It has, however, been pointed out (p. 266) that this supposed fourth nitrobenzoic acid may be nothing more than a mixture of two, or perhaps all three of the known modifications (o, m, and p), and its formation from the oily nitrobenzaldehyde—which, for anything yet shown to the contrary, may be itself a mixture of isomeric modifications (a view which is somewhat favoured by the change which it undergoes on distillation)—cannot be regarded as affording any further proof of the definite nature of the nitrobenzoic acid which melts at 127° .

Oxybenzoic Aldehyde, $\text{C}_6\text{H}_4\text{O}^2-\text{C}_6\text{H}_3\begin{smallmatrix} \text{OH} \\ \text{COH} \end{smallmatrix}$ (Reimer, *Deut. Chem. Ges.*

Ber. ix. 423; Reimer & Tiemann, *ibid.* 824). Two modifications of this compound are known, viz., salicylic aldehyde (1:2), and paraoxybenzoic aldehyde (1:4). They are obtained simultaneously by the action of chloroform on a strongly alkaline solution of phenol:



Fifteen parts of chloroform are gradually introduced by vigorous shaking into a (50°–60°) solution of 10 parts of phenol and 70 of sodium hydrate in 30–35 of water; an action speedily commences, the slightly yellow liquid soon becoming blue or reddish-violet, and finally deep red; and the temperature rises, so that, to avoid loss of chloroform, it is necessary to affix a reflux condenser. After half an hour's boiling the small quantity of chloroform that remains unacted on is distilled off, and hydrochloric or diluted sulphuric acid is cautiously added to the residue, until a strong acid reaction is manifest; a thick dark red oil, smelling strongly of salicylic aldehyde, is thus precipitated. On blowing steam through the whole, salicylic aldehyde and phenol pass over with the water-vapour, whilst a red resinous mass and a slightly yellow aqueous liquor remain in the distilling flask; this latter solution is filtered off through a wet filter, and, after cooling, well agitated with ether, which takes up the paraoxybenzoic aldehyde, and deposits it on evaporation in stellate needles, more or less tinged with yellow.

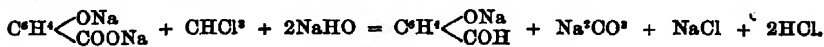
To prepare pure salicylic aldehyde from the distillate obtained as above, this distillate is shaken with ether, and the ethereal solution with acid sodium sulphite, whereby a crystalline compound is formed, from which the salicylic aldehyde may be separated by potash or soda.

This process affords the readiest means of preparing salicylic aldehyde. Other methods of obtaining this compound have been described in former volumes of this Dictionary, together with its properties and reactions (v. 167; 1st Suppl. 1008).

Nitrosalicylic Aldehydes, $\text{C}_6\text{H}_3\text{NO}(\text{OH})_2\text{COH}$.—When salicylic aldehyde is boiled with 3 parts of nitric acid diluted with twice its volume of water, an oil is obtained which solidifies to a crystalline mass on cooling. This mass consists of two isomeric mononitroderivatives, which may be separated by taking advantage of the difference in solubility of their barium compounds. The less soluble salt crystallises with two

molecules of water in beautiful yellowish-red prisms, and the nitroderivative separated from it, in small yellow prisms melting at 106° – 107° . The more soluble barium compound crystallises in yellow prisms containing at least 6 mols. of water: the corresponding nitro-compound forms needles which melt at 123° – 125° . Both the barium salts lose their water of crystallisation below 100° (G. Mazzara, *Gazz. chim. ital.* vi. 460).

Paraoxybenzoic Aldehyde, $\text{C}^{\circ}\text{COH.H.OH.H}^{\circ}$, is produced: 1. By heating anisaldehyde (methyl-paraoxybenzoic aldehyde) with dilute hydrochloric acid to 190° – 200° for three or four hours (Bücking, *Deut. Chem. Ges. Ber.* ix. 527). 2. Together with salicylic aldehyde, by the action of chloroform and alkalis on phenol in the manner above described. It is contained in the aqueous portion of the residue left on distilling the crude product thus obtained, and may be extracted therefrom by agitation with ether, the ethereal solution leaving it on evaporation in stellate groups of yellowish needles, which dissolve in cold, more readily in hot water, very easily in alcohol and ether. From the ethereal solution it may be completely extracted by agitation with an aqueous solution of acid sodium sulphite, and by recrystallisation from boiling water it is easily obtained in white needles. 3. Together with aldehyde-paraoxybenzoic acid (p. 289) by the action of chloroform on an alkaline solution of paraoxybenzoic acid:



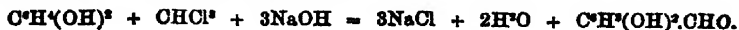
It remains in the mother-liquor from which the aldehyde-acid has crystallised out, and may be extracted therefrom by repeated agitation with ether. On distilling off the ether from the united ethereal extracts, there remains a yellowish mass consisting of the aldehyde, still mixed with considerable quantities of the aldehyde-acid, from which it may be separated by repeated fractional solution in small quantities of cold water, the less soluble portion, consisting chiefly of the aldehyde-acid, being each time rejected, and the solution evaporated to dryness.

Paraoxybenzaldehyde may be extracted from its aqueous solution by ether, and remains, on evaporating the ethereal solution, as a mass which melts at 114° – 115° . Its aqueous solution gives a faint bluish-violet colour with ferric chloride (Reimer a. Tiemann). It has an agreeable aromatic odour, reduces ammoniacal silver solutions, and forms crystalline salts with the alkali-metals. By fusion with potash it is converted into paraoxybenzoic acid, which is also formed, though not readily, by oxidising the aldehyde in solution. It unites with acid sodium sulphite, forming a compound which is very soluble in water, and crystallises from hot water in radiating colourless needles, melting at 111° – 112° , and resolidifying at 106° – 107° (Bücking).

Nitroparaoxybenzoic aldehyde, $\text{C}^{\circ}\text{H}^{\circ}(\text{NO}_2)(\text{OH})(\text{COH})$.—One of the two possible modifications of this compound is formed by heating paraoxybenzoic aldehyde with $1\frac{1}{2}$ times its weight of nitric acid, sp. gr. 1.20, diluted with 5 parts of water. The product is a dark brown or nearly black crystalline mass, impregnated with an oil, from which it may be separated by filtration and pressure between paper; and by crystallising the mass thus far purified from alcohol, with addition of animal charcoal, the nitro-aldehyde is obtained in long nearly colourless needles, melting, with slight sublimation, at 139° – 140.5° , and volatilising slowly with vapour of water. It dissolves in boiling water, and separates on cooling in small anhydrous needles, very sparingly soluble in ether, chloroform, and benzene. The aqueous solution gives a reddish colour with ferric salts.

Nitroparaoxybenzoic aldehyde exhibits strong acid properties, and decomposes carbonates. Its potassium salt, $\text{C}^{\circ}\text{H}^{\circ}(\text{NO}_2)(\text{OK})(\text{OOH}) + \text{H}^{\circ}\text{O}$, crystallises in golden-yellow plates, which give off their water at about 70° . The silver salt, $\text{C}^{\circ}\text{H}^{\circ}(\text{NO}_2)(\text{OAg})(\text{COH})$, is a canary-yellow precipitate. The solution of the potassium salt, mixed with cupric sulphate, gives, after some time, a greenish precipitate, which, when boiled with water and filtered, yields a liquid depositing, on cooling, crystals of nitroparaoxybenzoic aldehyde (G. Mazzara, *Gazz. chim. ital.* vii. 285).

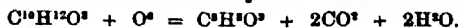
Protocatechuic Aldehyde, $\text{C}^{\circ}\text{H}^{\circ}\text{O}^{\circ} = \text{C}^{\circ}\text{COH.H.OH.OH.H}^{\circ}$. This compound, the only dioxybenzoic aldehyde at present known, was originally obtained by heating piperonal (methene-protocatechuic aldehyde) with dilute hydrochloric acid, or dichloro-piperonal with water (1st Suppl. 1024). It is also produced by heating vanillin, its monomethyl-derivative, with dilute hydrochloric acid; and by the action of chloroform on an alkaline solution of pyrocatechin:



Its properties and reactions have been described in the 1st Suppl. p. 976.

Methyl-protocatechuic Aldehyde or *Vanillin*, $C^8H^8O^3 = C^8COH.H.OCH^2.OH.H^2$. This substance, the fragrant constituent of the pods of *Vanilla aromatica*, in which it exists to the amount of about 2 per cent., is produced artificially: a. Together with an isomeric aldehyde, by the action of chloroform on an alkaline solution of guaiacol (methyl-pyrocatechin), $C^8H^4(OH)(OCH^3)$, just as protocatechuic aldehyde is formed from pyrocatechin.

β. By oxidation of coniferin or of coniferyl alcohol with chromic acid mixture:



Coniferyl
alcohol.



Coniferin.

γ. By oxidation of eugenol (in the form of its potassium salt) with potassium permanganate, a polymeride of eugenol being formed at the same time (Erlenmeyer, *Deut. Chem. Ges. Ber.* ix. 273):



Acetyl-eugenol yields by oxidation a large quantity of acetovanillic acid and a small quantity of acetovanillin, and these bodies when heated with potash are converted into vanillic acid and vanillin (Tiemann).

δ. Ethyl-vanillin, $C^{10}H^{12}O^3$, is formed by the action of water and emulsin on coniferin, and like its isomeride, coniferyl alcohol, is converted into vanillin by oxidation with chromic acid mixture (2nd Suppl. 1201).

Vanillin crystallises in stellate groups of colourless needles, melting at $80^\circ-81^\circ$, sparingly soluble in cold, more easily in hot water, very soluble in alcohol and ether. It forms crystallisable compounds with bases. Bromine converts it into monobromovanillin, which crystallises in yellow laminae melting at $160^\circ-161^\circ$. Vanillin is resolved by heating to $180^\circ-200^\circ$ with dilute hydrochloric acid into methyl chloride and protocatechuic aldehyde, and converted by fusion with potash into protocatechuic acid (comp. 2nd Suppl. 1201).*

Vanillin, treated with sodium-amalgam, is converted into vanillyl alcohol, $C^8H^{10}O^3 = C^8H^7(OH)(OCH^3).CH^2OH$, in the same manner as salicylic aldehyde is converted into saligenin. On adding sodium-amalgam to vanillin immersed in water, or very dilute alcohol, the vanillin immediately dissolves to a red liquid which afterwards turns yellow; and on adding fresh amalgam from time to time, leaving the liquid in contact with it for eight or ten days till no more vanillin can be detected in it, and then neutralising exactly with sulphuric acid, the liquid acquires a faint red colour, and begins to deposit white prismatic crystals, the crystallisation being completed in six or eight hours. These crystals consist of hydrovanilloin, $C^{10}H^{14}O^3 = 2C^8H^8O^3 + H^2$; they are insoluble in ether, very slightly soluble in hot water and boiling alcohol, easily soluble in alkalis, the compound being separated without alteration on neutralising the solution with an acid. Hydrovanilloin melts, with browning and decomposition, at $222^\circ-225^\circ$ (uncorr.). Strong sulphuric acid imparts to it a shining green colour; and then dissolves it with violet-red colour.

The liquid filtered from the hydrovanilloin contains vanillyl alcohol, which may be obtained by agitation with ether, as a yellowish undistillable oil, which gradually solidifies to a crystalline mass. Dilute acids convert it into a resin (vanilliretin), strong sulphuric acid dissolves it, forming a violet-red liquid (Tiemann, *Deut. Chem. Ges. Ber.* viii. 112").

Sodium-vanillin (obtained by evaporating an alcoholic solution of vanillin and sodium hydrate in equivalent proportions) yields with acetic anhydride a coumarin-like substance, which, when boiled with potash, is converted into an acid $C^{10}H^{10}O^3$, identical with the ferulic acid of *assafoetida* (Tiemann, *ibid.* ix. 52).

Ethyl-vanillin, or *Ethyl-methyl-protocatechuic Aldehyde*, $C^8H^7(OCH^3)(OC^2H^5).COH$, is obtained by heating potassium-vanillin with excess of ethyl iodide; also by the action of water and emulsin on coniferin (1st Suppl. 1201). When pure it forms colourless, prismatic, sometimes tabular crystals which are easily soluble in ether and alcohol, but very sparingly soluble in water. It melts at $64^\circ-65^\circ$, and sublimes without decomposition. It does not dissolve in potash or soda-ley more readily than in water. Its solutions in water or weak spirit are not affected by mineral acids. Strong sulphuric acid dissolves it without decomposition, forming a pale-yellow solution. With strong nitric acid it readily forms substitution-products.

Oxidising agents convert it into ethyl-vanillic acid, $C^{10}H^{12}O^4$, identical with the ethylmethylprotocatechuic acid obtained by oxidation of ethyl-eugenol (p. 291).

* The aldehyde $C^8H^8O^3$ is there called either vanillin or vanillic acid; but this latter name properly to methyl-protocatechuic acid, $C^8H^8O^3$, formed by oxidation of vanillin (p. 289).

Methyl-vanillin, or *Dimethyl-protocatechuic Aldehyde*, $C^8H^4(OCH^3)_2.COH$, is obtained in the same manner as the ethyl-compound. In the pure state it forms at ordinary temperatures a thick heavy pale-yellow oil. It boils without decomposition at 285° , and solidifies in a freezing mixture to needles which melt at $15^\circ-20^\circ$. With nitric acid it yields nitro-substitution-products. Oxidising agents readily convert it into dimethyl-protocatechuic acid.

Ethylvanillin and methylvanillin both possess a distinct odour of vanilla. Like vanillin itself, they are taken up from ethereal solution by acid sodium sulphite (Tiemann, *ibid.* viii. 1127).

Estimation of Vanillin in Vanilla.—An ethereal extract of vanilla, obtained by digesting 30–50 grams of the finely-chopped pods with three successive portions of ether (2½–3 litres in all), is evaporated to the bulk of 150–200 c.c. over a steam-bath, and the residue is briskly agitated for 10–20 minutes with 200 c.c. of a mixture of equal parts of water and a nearly saturated solution of acid sodium sulphite. After standing, the ethereal layer is separated, and the aqueous liquid, which now contains the whole of the vanillin, is placed in a flask so arranged that a current of steam can be driven through it. Dilute sulphuric acid (150 c.c. of a mixture of 3 vols. strong acid and 5 vols. water) is now added, and as soon as the effervescence, due to the escape of sulphur dioxide, has subsided, steam is passed through till the gas is completely driven off. The contents of the flask are then shaken with three successive portions (400–500 c.c. each) of ether, which takes up the vanillin, and the ethereal solution, after separation, is evaporated to 15–20 c.c. over the steam-bath, care being taken that the temperature at last does not rise above $50^\circ-60^\circ$. The residue is carefully transferred to a watch-glass and allowed to evaporate at the ordinary temperature, whereupon pure vanillin crystallises out and may be finally dried over sulphuric acid. Some estimations made to test this process showed a loss of 1–4 per cent. on the vanillin employed. The amount of vanillin in samples of commercial vanilla obtained from various sources was found to vary from 1·5 to 2·5 per cent. (Tiemann & Haarmann, *Deut. Chem. Ges. Ber.* viii. 1115).

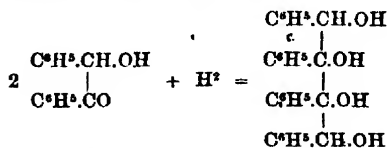
Methene-protocatechuic Aldehyde, or *Piperonal*, $C^8H^8O^3 = CH^2 \begin{smallmatrix} \diagup O \diagdown \end{smallmatrix} C^6H^3-CHO$.—

On the formation of this compound from the tetrabromide of piperic acid, see PIPERIC ACID. On its properties and reactions, see 1st Suppl. 947.; 2nd Suppl. 982.

BENZOÏN, $C^8H^8O^2$. *Decomposition by Heat*.—Benzoin when melted turns yellow and smells of benzoic aldehyde. When boiled it undergoes partial decomposition, and after three distillations, yields a mixture consisting principally of benzoic aldehyde, benzile, deoxybenzoin, and water. The same products are formed when the vapour of benzoin is passed through a tube heated to low redness (Zinin, *Deut. Chem. Ges. Ber.* vi. 1207).

Reduction.—Benzoin treated with a large excess of fuming hydriodic acid at 180° is converted into dibenzyl, C^8H^{14} . The production of dibenzyl is facilitated by previously converting the benzoin into a mixture of deoxybenzoin and toluylene hydrate by means of zinc and hydrochloric acid, and then heating the mixture to 180° with hydriodic acid (Goldenberg, *Ciebig's Annalen*, clxiv. 333). The same result has been obtained by Limpricht & Schwanert.

By treating benzoin in weak alcoholic solution with sodium-amalgam, a solution is obtained containing hydrobenzoin, deoxybenzoin, and benzoin-pinacone, $C^{12}H^{20}O^4$, this last substance being formed by the reaction:



Zinc and hydrochloric acid also cause the conversion of benzoin into this product; the best yield is obtained by dissolving benzoin in hot alcohol to saturation, adding granulated zinc, and then adding, in very small quantities at a time, a mixture of alcohol and hydrochloric acid. Benzoin may with advantage be added at intervals, so as to keep the solution saturated whilst the benzoin-pinacone separates out.

Benzoin-pinacone melts at 208° , is insoluble in water, but dissolves in ether and hot alcohol, not in cold alcohol.

According to Zagumenny (*Deut. Chem. Ges. Ber.* vii. 1851) the product of the action of sodium-amalgam on benzoin is not benzoin-pinacone, but is probably identical with the compound $C^{12}H^{20}O^2$, which Limpricht & Schwanert obtained by the action of

sodium ethylate on benzene (2nd Suppl. 176). Zagumenny has obtained the same compound by treating deoxybenzoin with zinc and caustic potash.

BENZONITRANILIDE, $C^6H^4(NO^2).NH.CO.C^6H^5$. See **BENZANILIDE** (p. 157).

BENZONITRIL or **PHENYL CYANIDE**, $C^6H^5N \equiv NC(C^6H^5)$. On the formation of this compound by heating benzoic acid with potassium thiocyanate, see 2nd Suppl. 106.

Nitrobenzonitrile, $NC.C^6H^4.NO^2$, and **Amidobenzonitrile**, $NC.C^6H^4.NH^2$ (Fricke, *Deut. Chem. Ges. Ber.* vii. 1321).

The **nitrobenzonitrils** are formed by the action of phosphoric anhydride on the corresponding nitrobenzamides, $NH^2.C^6H^4.NO^2$, which are themselves produced by the action of ammonia on the corresponding nitrobenzoyl chlorides; and the amidobenzonitrils are obtained by reducing the nitrobenzonitrils with tin and glacial acetic acid.

Metanitrobenzonitril, $C^6.CN.H.NO^2.H^2$, forms long colourless needles melting at 115° , easily soluble in alcohol, ether, chloroform, and glacial acetic acid, sparingly soluble in water. Its properties agree with those of the nitrobenzonitril (m. p. 116°) which Engler obtained by the action of fuming nitric acid on benzonitril (1st Suppl. 528).

Paranitrobenzonitril, $C^6.CN.H.H.NO^2.H^2$, crystallises in shining laminae melting at 147° (139° Engler), easily soluble in hot alcohol, glacial acetic acid, and chloroform.

Metamidobenzonitril, identical with the compound which Griess obtained by the action of cyanogen on amidobenzonic acid, and Hofmann by nitration and amidation of benzonitril (1st Suppl. 626), forms long needles melting at 52° – 53° , slightly soluble in water, easily in alcohol and chloroform. Its **hydrochloride** crystallises in colourless very soluble prisms; the **nitrate** and **sulphate** are very soluble in water and in alcohol, the former crystallising in large yellowish scales, the latter in long colourless needles.

Paramidobenzonitril, $C^6.CN.H.H.NH^2.H^2$, crystallises in small colourless needles melting at 110° (at 74° according to Engler), easily soluble in alcohol, ether, and boiling water. The **hydrochloride** forms small needles easily soluble in water and in alcohol; the **nitrate**, small laminae of equal solubility; the **sulphate** small colourless needles (Fricke).

BENZONITROTOLUIDIDE, $C^6H^4N^2O^2 = N \begin{Bmatrix} C^6H^5O \\ C^6H^5NO^2 \\ H \end{Bmatrix}$. This body is formed

by the action of benzoyl chloride, directly, or better, in ethereal solution, on nitrotoluidine:—



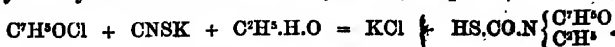
The ether having been driven off and the nitrotoluidine hydrochloride dissolved out by boiling water, the residual benzo-nitrotoluidide is purified by several recrystallisations from boiling alcohol. It crystallises in pale yellow prisms, melting at 172° , and, if carefully heated, sublimes unaltered. It is soluble in alcohol, ether and benzene, especially when these liquids are heated, insoluble in dilute acids and in strong hydrochloric acid, but soluble in oil of vitriol. Boiling soda-solution has but little effect upon it, although it is easily acted upon by alcoholic potash. Nascent hydrogen converts benzonitrotoluidide, by substitution of NH^2 for NO^2 , into benzoyl-tolylene-diamine or benzoyl-diamidotoluene. $C^6H^5 \begin{Bmatrix} NH^2 \\ NH(C^6H^5O) \end{Bmatrix}$ (C. A. Bell, *Chem. News*, xxx. 202).

BENZOXYALOBENZENE, $C^6H^5(C^6H^5O)N^2O$. See **BENZENE (OXYAZO-)**, 2nd Suppl. 151.

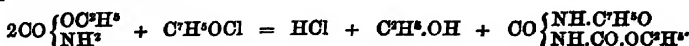
BENZOYL CHLORIDE, $C^6H^5OCl = C^6H^5.COCl$. This compound solidifies at the temperature of a mixture of ice and salt (Sperlich & Lippmann, *Wien. Akad. Ber.* [2 Abth.], lxii. 613; Lieben, *Liebigs Annalen*, clxxviii. 43). The solid chloride melts at -1° (Lieben).

Benzoyl chloride is decomposed by *zinc*, with evolution of hydrochloric acid and formation of a brown resin. A mixture of benzoyl chloride and benzene or toluene is also attacked by zinc, with separation of hydrochloric acid, the greater part of the benzoyl chloride, in fact, decomposing in the same manner as if the benzene or toluene were not present. In presence of benzene, there is formed, together with much benzoic acid and very little benzophenone, a compound which crystallises from alcohol in long thick red needles, and melts at about 140° – 146° (Zincke, *Deut. Chem. Ges. Ber.* v. 137).

Potassium thiocyanate acts on benzoyl chloride in alcoholic solution, forming crystals of benzoyl-ethyl-thiocarbamic acid (Lossner, *see* p. 312):—



Benzoyl chloride and urethane, heated together to 150°–160°, yield the compound $C^{11}H^{12}N^2O^4$ in brilliant crystals melting at 163°. It is probably a benzoylallopphanic ether produced as follows:—



Benzoyl chloride and oxamethane yield hydrochloric acid, carbon dioxide, benzoic acid, and ethyl benzoate (Kretschman, *Deut. Chem. Ges. Ber.* viii. 103).

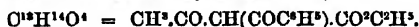
Benzoyl chloride and cyanamide, heated together, or mixed in ethereal solution, do not yield benzoyl cyanide, as might be expected, according to the equation



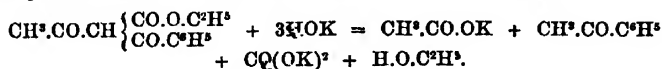
but benzoyl chloride and dry sodium cyanide, $CN.N(HNa)$, give benzoyl-ammeline, benzonitril, carbon dioxide, and sodium chloride; and the same substances in presence of ether give benzoyl cyanide and sodium chloride (Gerlich, *J. pr. Chem.* [2], xiii. 270). See CYANAMIDE.

With dinitrophenol, benzoyl chloride forms a benzoyl-derivative which crystallises in needles and melts at 201°. Alcoholic potash resolves this compound into dinitrophenol and benzoic acid (Goldstein, *Bull. Soc. Chim.* [2], xxvi. 294).

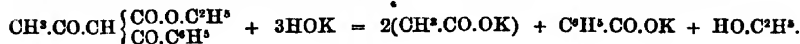
BENZOYL-ACETOACETATE, ETHYLIC,



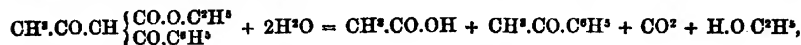
This ether, already noticed (p. 13), has been further examined by J. Bonnè (*Liebig's Annalen*, clxxvii. 1). It is prepared by digesting a solution of ethylic acetosodacetate in ether or benzene in a reflux apparatus with an equivalent quantity of benzoyl chloride. The action is energetic, and the vessel must be cooled with ice. The separation of sodium chloride takes place immediately, and the reaction goes on to the end without external heating. By filtering and washing the separated sodium chloride with ether, a yellow liquid is obtained which, on evaporation of the solvent, leaves a brown oil; and by repeatedly dissolving this product in alcohol, precipitating with water, and finally drying in a vacuum till the weight becomes constant, the benzoyl-aceto-acetic ether is obtained as a thickish liquid having a faint but agreeable odour, a sp. gr. of 1.14 at 21.5° (water at 17.5° = 1) and decomposing when somewhat strongly heated, yielding benzoic ether and benzoic acid, together with other products not examined. By saponification with alcoholic potash, it yields methyl-phenyl ketone, potassium acetate and carbonate, and ethyl alcohol, thus:—



A little benzoic acid is, however, produced by a subsidiary reaction, probably:—

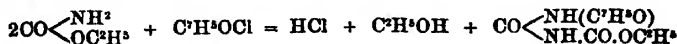


A similar decomposition is brought about by heating with water to boiling for a few hours, the chief reaction being—



whilst a little benzoic acid is also produced by a subsidiary reaction.

* **BENZOYL-ALLOPHANIC ETHER**, $C^{11}H^{12}N^2O^4$, is produced, together with alcohol, hydrochloric acid, and carbon dioxide, by the action of 1 mol. benzoyl chloride on 2 mols. of urethane:—



The carbon dioxide appears to be formed by a secondary reaction. Benzoyl-allophanic ether melts at about 163° (Kretschmar, *Deut. Chem. Ges. Ber.* viii. 104).

BENZOYL-AMIDODIPHENYL, $C^{12}H^9.NH(C^6H^5O)$. See DIPHENYL.

BENZOYL-AMIDOPHENOLS, $C^6H^4(OH)NH.CO.C^6H^5$ (H. Morse, *Deut.*

midophenol hydrochloride, obtained from volatile to 150° with benzoyl chloride, a benzoyl-amidophenol from alcohol in colourless or reddish plates and prisms, having an agreeable odour and melting at 108°. With fuming nitric acid it yields a dinitro compound in straw-yellow slender needles melting at 103°; and this, when treated with tin and hydrochloric acid, is converted into the stannochloride of a diamido-compound which crystallises in colourless needles, permanent only when kept under strong hydrochloric acid. By removing the tin from this double salt, the hydrochloride of a base is obtained, crystallising in laminae, and from this salt the base itself is precipitated by ammonia in needles which are not altered by exposure to light.

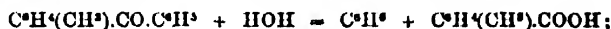
Non-volatile nitrophenol (m. p. 114°) yields by similar treatment a nitrobenzoyl-amidophenol, in the form of a dense colourless crystalline mass which melts with partial decomposition at 139°. It is insoluble in water, slightly soluble in cold alcohol, and decomposed by boiling alcohol.

BENZOYL (DI-)BENZENE, $C^6H^5CO \cdot C^6H^5$. Two modifications of this compound are formed by oxidation of the corresponding di-benzyl-benzenes. See DI-BENZYL-DERIVATIVES.

BENZOYL-BENZOIC ACID, $C^6H^5CO \cdot C^6H^4COOH$. Three modifications of this acid, α , β , γ , are produced simultaneously by the action of chromic acid on benzyl-toluene, prepared by the action of zinc on a mixture of toluene and benzyl chloride. The first, which crystallises in plates or needles melting at 194°–195°, was discovered by Zincke (2nd Suppl. 177); the second by Plascuda, a. Zincke (*Deut. Chem. Ges. Ber.* vi. 908), and the third by Rotering (*Inaug. Dissert.* Berlin, 1875; *Deut. Chem. Ges. Ber.* viii. 319).

The formation of these three acids shows that benzyl-toluene, prepared as above, is itself a mixture of three isomeric compounds; and this conclusion is strengthened by the fact that the benzyl-toluene, when partially oxidised, yields a mixture of a solid and a liquid tolyl-phenyl ketone, $CO \cdot C^6H^4CH_3$, the former convertible by

further oxidation into α -benzoyl-benzoic acid, the latter into a mixture of the β and γ acids. Now the solid ketone is resolved, by heating with soda-lime, into benzene and *para*-toluic acid:—



hence it is itself a *para*-compound, having the methyl of the group $C^6H^4(CH_3)$ in the *para*-position with respect to the CO. Moreover this ketone is converted by oxidation into α -benzoyl-benzoic acid (m. p. 194°–195°) which is, therefore, also a *para*-compound:—



Liquid tolyl-phenyl ketone, on the other hand, yields by oxidation a mixture of β and γ -benzoyl-benzoic acids, the former of which is most probably the *ortho*-compound, inasmuch as it is formed in comparatively large quantity, together with the *para*-acid, by oxidation of crude benzyl-toluene, and, moreover, is converted by zinc and hydrochloric acid into a benzhydrol-benzoic acid, $C^6H^5CH_2COOH$, which is very easily resolved into water and an anhydride—a mode of decomposition which is known to take place with *ortho*-compounds (e.g. salicylic acid) more readily than with *meta*- or *para*-compounds.

The three benzoyl-benzoic acids are best obtained, according to Rotering, by oxidising benzyl-toluene with chromic acid mixture, and the separation of the α -acid from the other two may be effected, as recommended by Plascuda a. Zincke, by means of the barium salts, that of the α -acid being the least soluble of the three, and crystallising out first. The mixture of the β and γ -acids obtained from the mother-liquors may be freed from the last traces of the α -acid by converting the barium salt into calcium salts, and treating these with hot absolute alcohol; the still adhering α -salt then remains undissolved, together with the calcium salt of another acid (probably a mixture) melting at 140°–145°. Lastly, the mixture of β and γ -acids thus purified is repeatedly crystallised from dilute alcohol, whereupon the β -acid crystallises out pure,

and the last mother-liquors yield, together with this acid, small crystals of a different shape, which, when purified by repeated crystallisation from large quantities of boiling water, constitute the γ -acid.

α and β benzoyl-benzoic acids are reduced by the action of zinc and hydrochloric acid on their alcoholic solutions to the corresponding benzhydryl-benzoic acids, $C^{10}H^{12}O^2$, and by the action of sodium-amalgam on their aqueous solutions, first into the latter and then into benzyl-benzoic acids, $C^{11}H^{12}O^2$ (pp. 315, 321).

α - or Para-benzoylbenzoic acid.—The properties of this acid and of some of its salts have been already described (2nd Suppl. 177). The following additional salts have been obtained by Plascuda (*Deut. Chem. Ges. Ber.* vii. 986). The *potassium salt* forms tufts of slender needles, less soluble than the corresponding β -salt. The *ammonium salt* forms long thick needles, not very soluble in water; the solution easily loses ammonia and becomes acid. The *copper salt* is a green crystalline precipitate, soluble in hot water. The *methylic ether*, $C^{11}H^{10}O^2.CH^3$, forms large shining leaflets which melt at 107° , and are less soluble than the β -ether. The *ethylic ether*, $C^{11}H^{10}O^2.C^2H^5$, forms tabular monoclinic crystals melting at 52° ; water separates it in shining scales from its alcoholic solution.

By nitration of α -benzoyl-benzoic acid, a dinitrobenzoyl-benzoic acid is obtained, isomeric with that which results from the oxidation of dinitrobenzyl-toluene. It separates from water in shining leaflets which melt at 240° , and are easily soluble in alcohol or acetic acid, but less soluble in water. The *ammonium salt* forms shining, easily soluble scales, while the *copper salt* separates from hot water in shining bluish needles. The *zinc salt* is amorphous, and the *barium salt*, $[C^{11}H^7O^4(NO^2)^2]^2Ba + H^2O$, forms nodular tufts of needles very slightly soluble in water. The *calcium salt* crystallises in shining white leaflets which give off their water at 120° .

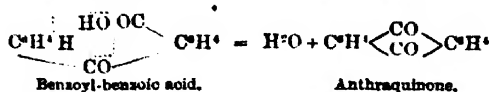
β - or Orthobenzoyl-benzoic acid crystallises from hot water, in which it is much more soluble than the α -acid, in long broad needles consisting of aggregates of prismatic crystals. Before these needles form, the solution becomes turbid from the separation of oil-drops. By slow evaporation of an aqueous or slightly alcoholic solution, it is obtained in well-defined prisms, apparently monoclinic, but frequently having a rhombohedral aspect. The acid dried over oil of vitriol contains 2 mols. H^2O , which escape at 100° . The hydrated acid melts at $85^\circ-87^\circ$, the dried acid at $127^\circ-128^\circ$.

Potassium orthobenzoylbenzoate is easily soluble in water, insoluble in alcohol, and crystallises in broad needles. The *ammonium salt* is easily soluble in water, and forms needles having a satiny lustre. The *barium salt*, $(C^{11}H^7O^4)^2Ba$, is easily soluble in water, and is obtained, by evaporation of its aqueous solution, as a vitreous mass; it dissolves in hot alcohol, and separates therefrom in indistinct nodules. The *calcium salt*, $(C^{11}H^7O^4)^2Ca$, is still more soluble, and not crystallisable even from alcohol; it may be advantageously used for the separation of the α - and β -acids. The *silver salt*, $C^{11}H^7O^4Ag$, crystallises from a large quantity of hot water in small needles. The *copper salt*, $(C^{11}H^7O^4)^2Ca + H^2O$, is a scaly crystalline powder crystallising in laminae from hot alcohol, and melting under hot water. The *zinc salt*, $(C^{11}H^7O^4)^2Zn + 2H^2O$, is a flocculent precipitate which melts under hot water; after drying it melts at 140° .

The *methylic ether*, $C^{11}H^{10}O^2.CH^3$, is easily soluble in water and in alcohol, and crystallises in fine rhombic prisms with oblique dihedral summits, not unlike crystals of augite. It melts at 52° , and remains fluid for a long time. The *ethylic ether*, $C^{11}H^{10}O^2.C^2H^5$, forms rhombohedral crystals growing together into prisms 3 or 4 centimeters long. It dissolves easily in alcohol and ether and melts at 58° .

By the action of fuming nitric acid, or a mixture of this acid with strong sulphuric acid, the β -acid is converted into a mixture of resinous nitro-acids, which show no tendency to crystallise.

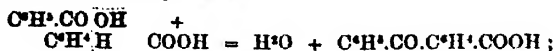
Conversion of β -benzoyl-benzoic acid into Anthraquinone.—This acid heated, with phosphoric anhydride gives up a molecule of water, and yields a distillate of anthraquinone, $C^{14}H^8O^2$. The nature of the change is indicated by the following equation, in which the dotted square shows the atoms of H and O which are removed:



The best mode of proceeding is to heat a mixture of 1 pt. β -benzoyl-benzoic acid, and 2 pts. phosphoric anhydride with sand to 200° for some hours, and then extract the anthraquinone with benzene; the anthraquinone thus obtained amounts to 26 per cent. of the theoretical quantity.

Parabenzoyl-benzoic acid treated in the same manner does not yield anthraquinone.

Small quantities of anthraquinone are also produced by distilling benzoic acid with phosphoric anhydride, $\frac{1}{2}$ mols. of benzoic acid giving up 1 mol. water, and coalescing to form β -benzoyl-benzoic acid: *



which then, by loss of another molecule of water, is converted into anthraquinone.

The formation of anthraquinone by the distillation of calcium benzoate depends on a similar series of changes, CaH^2O^2 being separated instead of H_2O . It is probable also that anthraquinone might be formed by distillation of the calcium salt of β -benzoyl-benzoic acid (Behr & van Dorp, *Dent. Chem. Ges. Ber.* vii. 578).

γ or *Metabenzoyl-benzoic acid*, the separation of which from the α - and β -acids has been already described (p. 309), is obtained from the solutions of its salts in the form of a loose white powder. It dissolves easily in alcohol and ether, in water about as readily as the α -acid. It crystallises from water or dilute alcohol in long shining, concentrically grouped needles, melts at 162° , and immediately solidifies to a crystalline mass on cooling.

The γ -benzoyl-benzoates are not very well defined. The barium salt, $(\text{C}^6\text{H}^5\text{O}^2)^2\text{Ba}$, separates, on concentrating, its solution, or on recrystallising it from water or dilute alcohol, in which it is very soluble, as a granular powder. The calcium salt, $(\text{C}^6\text{H}^5\text{O}^2)^2\text{Ca}$, exhibits similar characters. The silver salt, $\text{C}^6\text{H}^5\text{O}^2\text{Ag}$, is a white amorphous insoluble powder, but little altered by light.

The acid melting at 140° – 145° , mentioned above (p. 309), as a bye-product of the preparation of the three benzoyl-benzoic acids, appears also to have the composition $\text{C}^6\text{H}^5\text{O}^2$; but as it does not form well-characterised salts, or melt at a constant temperature, Rotering regards it as a mixture.

Benzhydryl-benzoic Acids, $\text{C}^6\text{H}^5\text{O}^2 = \text{C}^6\text{H}_5\text{CHOH.C}^6\text{H}_5\text{COOH}$. These acids (α and β) are produced by boiling the corresponding benzoyl-benzoic acids in alcoholic solution with zinc and hydrochloric acid. The α -acid already described (2nd Suppl. 177), crystallises in needles, melts at 164° – 165° , and decomposes at a higher temperature (Zincke).

The β -acid appears to be incapable of existing in the free state, as at the moment of its formation, it splits up into H_2O and the anhydride, $\text{C}^6\text{H}^5\text{O}^2$, or $\text{C}^6\text{H}_5\text{—CH—C}^6\text{H}_5$. This compound is obtained by boiling the alcoholic solution of



β -benzoyl-benzoic acid with zinc and hydrochloric acid for several days, and separates on cooling from the hot-filtered solution in the form of a white powder. It is insoluble in water, whether cold or hot, slightly soluble in cold, freely in hot absolute alcohol and ether, and separates therefrom in cruciform groups of prismatic needles. From dilute acetic acid it separates in groups of leaflets. It melts at 115° , solidifies immediately on cooling, and when very strongly heated, sublimes in small shining laminae resembling benzoic acid. It differs from α -benzhydryl-benzoic acid, in not exhibiting any characteristic coloration with strong sulphuric acid. By oxidising agents it is reconverted into β -benzoyl-benzoic acid. The anhydride is completely indifferent to alkaline carbonates, and is but slightly attacked even by caustic alkalis and alkaline earths.

The β -benzhydryl-benzoates thereby produced are not distinctly characterised, and have but little stability, being readily decomposed by acids with separation of the anhydride. They are most stable in alcoholic solution, and in presence of excess of base. The potassium salt, $\text{C}^6\text{H}^5\text{O}^2\text{K}$, was prepared by boiling the anhydride for a considerable time with potassium carbonate.† On evaporating the solution over the water-bath there remained an oily liquid, which became crystalline on being dried and triturated with absolute alcohol; and by repeatedly treating this mass with the benzhydryl-benzoate was dissolved out, while potassium carbonate remained behind. On evaporating the alcohol, the salt remained as an amorphous vitreous mass, which dissolved in alcohol, forming a clear solution, becoming turbid and alkaline on addition of water. The barium salt was prepared by digesting the

* A similar condensation possibly takes place when benzoic acid is fused with potash. Berthel, in fact, has shown (*Berlin's Annalen*, cliiv. 188) that in this case there is formed, together with other products, a body having the composition of benzoyl-benzoic acid; the properties of this body do not, however, agree with those of either α - or β -benzoyl-benzoic acid (Behr & van Dorp).

† This is not consistent with the previous statement that the anhydride is 'completely indifferent' to alkaline carbonates.

anhydride with excess of barium hydrate on the water-bath, and removing the excess of baryta by carbonic acid. On evaporating the filtrate, there remained an indistinctly crystalline powder, the amount of barium in which agreed with the formula $(C^6H^{11}O^8)^2Ba.2C^6H^{10}O^2$; the filtrate appeared to contain the neutral barium salt. On repeating the experiment in an alcoholic solution, there remained on evaporation an amorphous glassy substance, which redissolved in alcohol without turbidity, and had approximately the composition $(C^6H^{11}O^8)^2Ba$. On triturating it with water, a white crystalline precipitate was formed, containing only half the original amount of barium. The solution of the calcium salt, prepared in like manner, left on evaporation a residue of almost pure anhydride. The silver salt also could not be prepared.

The anhydride is not attacked by ammonia, either aqueous or alcoholic, even at 150° . Heated to 130° – 140° with phosphorus pentachloride, it yields anthraquinone and a mixture of chloranthracenes, which melts at 200° – 215° , exhibits a fine blue fluorescence in alcoholic solution, but is not resolvable into its individual constituents. This reaction affords further evidence of the relation of β -benzoyl-benzoic acid (and therefore of orthotolylphenyl-ketone and orthobenzyl-toluene) to anthracene.

Dibenzoyl-benzoic Acids, $C^{12}H^{10}O^4 = \begin{matrix} C^6H^5CO \\ C^6H^5CO \end{matrix} \begin{matrix} C^6H^5CO^2H, \text{ or } \textit{Benzo-benzoyl-benzoic acids}, C^6H^5-CO-C^6H^5-CO-C^6H^5-CO^2H. \end{matrix}$ Two acids (α and β) of this composition are formed, together with an acid having the composition $C^{12}H^{10}O^4$, by oxidation of the hydrocarbon (or hydrocarbons) $C^{12}H^{12}$, obtained as a secondary product in the preparation of benzyl-toluene. The α -acid is resinous, melts at 80° – 82° , and forms uncrystallisable mostly resinous salts. The β -acid crystallises in small needles, melting at 210° – 212° , insoluble in water, easily soluble in alcohol, ether, and chloroform. Its salts are all sparingly soluble. The ethylic ether crystallises in white needles melting at 106.5° – 107° .

The α -acid distilled with baryta does not yield any definite products. When fused with potassium hydrate it gives off an odour of diphenyl, and yields a large quantity of benzoic acid, together with a small quantity of an infusible acid, $C^{12}H^{10}O^4$, isomeric with that which is obtained, as above-mentioned, by the direct oxidation of the hydrocarbon $C^{12}H^{12}$ (Weber & Zinck, *Deut. Chem. Ges. Ber.* vii. 1153).

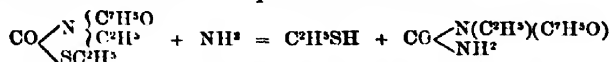
BENZOYL-DIMETHYLANILINE, $C^{14}H^{13}NO = C^6H^5.CO.C^6H^4.N(CH^3)^2$, is formed by heating to 180° – 200° for six or eight hours a mixture of benzoic acid, dimethylaniline and phosphoric anhydride, and purified by shaking its ethereal solution successively with alkali and acid, and crystallising from petroleum ether. It melts at 38° , boils at 330° – 335° , is destitute of basic properties, forms a crystallised dinitro-derivative melting at 142° , and a crystalline bromo-derivative (O. Fischer, *Deut. Chem. Ges. Ber.* x. 968).

BENZOYL-DITOLYLAMINE. See TOLYLAMINES.

BENZOYL-ETHYL-CARBAMIC ACID, $C^6H^9NO^3 = CO \begin{matrix} \text{N}(C^2H^5)(C^2H^5O) \\ \text{OH} \end{matrix}$

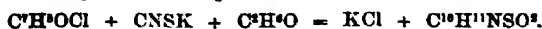
is formed by the action of lead oxide on benzoyl-ethyl-thio-carbamic acid (*infra*); the change consisting in the replacement of the sulphur-atom in the latter by oxygen. It forms hard white needles, melting at 110° , easily soluble in alcohol and ether, but sparingly soluble in water. When treated with potassium hydrate, it yields potassium benzoate and carbonate as well as alcohol and ammonia. The potassium salt is a white sandy powder. Ethyl bromide, under pressure, transforms it into benzoic ether, ethylamine, ether, and carbonic anhydride (Lössner).

BENZOYL-ETHYL-CARBAMIDE, $C^{10}H^{12}NO^2$, is formed, together with mercaptan, by passing ammonia to saturation into the ethylic ether of benzoyl-ethyl-sulphocarbamic acid mixed with an equal volume of alcohol:



It is neutral, crystallises in rhombohedrons, and does not combine with sulphuric acid (Lössner).

BENZOYL-ETHYL-THIOCARBAMIC ACID, $C^6H^{11}NSO^2 = CO \begin{matrix} \text{N}(C^2H^5)(C^6H^5O) \\ SH \end{matrix}$ (Linné Lössner, *J. pr. Chem.* [2], x. 235). This acid is formed by the action of benzoyl chloride on potassium thiocyanate in alcoholic solution:



Benzoyl chloride is gradually added to a moderately concentrated solution of potassium thiocyanate in absolute alcohol contained in a large flask, till a distinct white precipi-

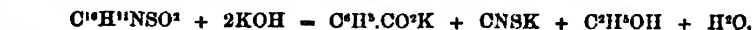
tate of calcium chloride is produced. The potassium thiocyanate should be in slight excess, otherwise some of the benzoyl chloride will be converted into ethyl benzoate. The reaction is attended with considerable rise of temperature and tumefaction of the liquid. On decanting the alcoholic liquid, and pouring in water, with constant stirring, till it becomes milky, the benzoyl-ethyl-thiocarbamic acid separates in hard yellow crystals, which must be washed on a filter with water, till the wash-water is no longer reddened by a ferric salt, then pressed between paper, dissolved in alcohol of 80 per cent. and precipitated by water as before.

The crystals thus obtained are well-defined, rather long, hard prismatic needles of almost sulphur-yellow colour, very slightly soluble in water, easily in alcohol and ether. They melt at 73°-74°.

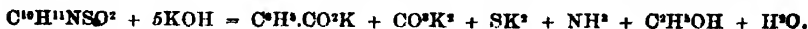
Benzoyl-ethyl-thiocarbamic acid is resolved by heat into ethyl-mercaptan, benzonitril, and carbon dioxide:



Heated with potash-solution it yields benzoate, thiocyanate, sulphide, and carbonate of potassium, together with alcohol and ammonia; thus:



and



These reactions establish the constitutional formula above given.

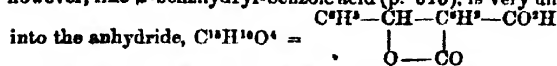
Potassium Benzoyl-ethyl-thiocarbamate is best prepared by adding a solution of potassium hydrate in alcohol to an alcoholic solution of the acid, and recrystallising from alcohol. It crystallises in small needles, is very soluble in water, less soluble in alcohol and ether.

The silver salt is white and flocculent, and turns black on boiling; the lead salt has a similar appearance, and is also unstable. Mercuric chloride produces a finely divided white precipitate, which may be boiled in water without decomposition. Copper sulphate gives rise to a grayish-green precipitate, which blackens on heating.

The ethylic ether is formed by cohobating the potassium salt with ethyl bromide, as a yellow heavy oil, which cannot be distilled without decomposition. Treated with potassium hydrate, it yields benzoate and carbonate of potassium, ammonia, alcohol, and mercaptan. When the ether is heated in a tube to 105°, crystals melting at 128°-129° are formed, which have not been investigated.

BENZOYL-ISOPHTHALIC ACID. $C^6H^5H^5O^2 = C^6H^5.CO.C^6H^4(CO^2H)^2$ (Blatzbocker, *Deut. Chem. Ges. Ber.* ix. 1761). This acid is produced by the oxidising action of chromic acid on benzyl-isoxylene (prepared from commercial xylene, and probably a mixture of meta- and para-xylene). It is sparingly soluble in water, chloroform, and toluene, freely in alcohol and ether. On adding water to its alcoholic solution, it separates in crystalline crusts melting at 278°-280°. The potassium salt, $C^6H^5.CO.C^6H^4(CO^2)^2Ba + H^2O$, separates in glistening needles from its aqueous solution on addition of alcohol. The calcium salt, $C^6H^5.CO.C^6H^4(CO^2)^2Ca + H^2O$, forms needles or plates. The silver salt is a white insoluble powder. By treating it with ethyl iodide the ethylic ether is obtained, crystallising in needles and melting at 94°. The methylic ether is a similar body melting at 117°-118°.

Benzoyl-isophthalic acid treated with zinc and hydrochloric acid is converted into benzhydryl-isophthalic acid, $C^6H^5H^5O^2 = C^6H^5.CHOH.C^6H^4(CO^2H)^2$, which, however, like β -benzhydryl-benzoic acid (p. 316), is very unstable, and at once changes



BENZOYL-MORPHINE. See MORPHINE.

BENZOYL-NAPHTHYLAMIDE. See NAPHTHYLAMIDE.

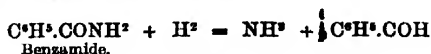
BENZOYL-SULPHUREA or **BENZOYL-THIOCARBAMIDE.** See THIOCARBAMIDES, under CARBAMIDES.

BENZOYL-TOLYLENE-DIAMINE. See TOLYLENE-DIAMINES.

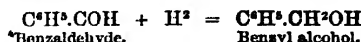
BENZYL. As radicle $C^6H^5 = -OH^2(C^6H^5)$. *Phenyl-methyl.*—In the free state, $C^6H^5H^5 = C^6H^5-CH^2-C^6H^5$. See DIBENZYL.

BENZYL ALCOHOL, $C^6H^5O = C^6H^5.CH^2OH$. This alcohol occurs in small quantity, together with benzaldehyde, prussic acid, and a fragrant resin, in the volatile oil of cherry-laurel (Tilden, *Pharm. J. Trans.* [3], v. 761).

It is formed, and may perhaps be advantageously prepared, by the action of water and sodium-amalgam on benzamide:



and



(Guareschi, *Gazz. chim. ital.* iv. 465).

Benzyl alcohol heated to 140° with hydriodic acid (b. p. 127), and phosphorus, is reduced to toluene, together with very small quantities of high-boiling compounds. In presence of phosphorus, this reaction may be carried out even with a quantity of hydriodic acid insufficient for the formation of benzyl iodide, provided the temperature be raised to 170°–190° (Graebe, *Deut. Chem. Ges. Ber.* viii. 1054).

BENZYL CYANIDE, $\text{C}^6\text{H}^5\text{.CH}^2\text{.CN}$. This compound, heated for several days on the water-bath in a reflux apparatus with an alcoholic solution of potassium hydrosulphide, is converted into *α*-toluamide or phenylacetamide. In presence of phosphorus, this reaction may be obtained in dazzling white crystals by distilling off the alcohol after the evolution of ammonia has ceased, washing the residual brown mass with cold water, and recrystallising it from alcohol, with addition of animal charcoal (Weddige, *J. pr. Chem.* [2], vii. 99).

BENZYL HALOID ETHERS OF.—These ethers, when acted upon by silver nitrite, do not yield nitro-derivatives of toluene. On treating the iodide in this manner, nitrogen dioxide is given off, and the benzyl is oxidised, yielding chiefly benzaldehyde and benzoic acid (van Renesse, *Deut. Chem. Ges. Ber.* ix. 1454). Similar results have been obtained by H. Brunner (*ibid.* 744). With benzyl chloride and silver nitrite, non-azotised bodies of high boiling point are obtained, including anthracene, together with benzaldehyde and benzoic acid.

Bromobenzyl Bromide, $\text{C}^6\text{H}^5\text{Br.CH}^2\text{Br}$ (C. I. Jackson & W. Lowry, *Deut. Chem. Ges. Ber.* viii. 1672; Jackson, *ibid.* ix. 931). The three modifications of this compound, differing from one another by the relative positions of the radicles Br and CH^2Br , are obtained by passing bromine-vapour into the corresponding bromotoluenes at the boiling heat.

Parabromobenzyl bromide, $\text{C}^6\text{H}^4\text{Br.H.H.Br.H}^2$, is prepared by boiling the mixture of para- and ortho-bromotoluene formed by the action of bromine on toluene in the cold, and passing into the boiling liquid the vapour of an equal weight of bromine. The product is purified by distillation with steam. It crystallises from alcohol in needles, having an agreeable aromatic taste and melting at 61°. The vapour strongly attacks the eyes, nose, and throat. The substance sublimes in needles and burns with a smoky, green-bordered flame. It is violently attacked by a mixture of potassium bichromate and sulphuric acid, and yields an acid melting at 239°–240°.

Metabromobenzyl bromide is formed by passing the vapour of bromine into boiling metabromotoluene. The yield is very small. It crystallises in white needles, of an agreeable odour distinct from that of the para-compound. It melts at 41°. Volatilises very easily in ether-vapour. By oxidation with chromic acid it yields an acid which crystallises in needles and melts at 161°.

Orthobromobenzyl bromide is obtained by passing the vapour of bromine into boiling orthobromotoluene. In this case the bromine is absorbed much less readily than in either of the previous cases. The product could not be fully purified, owing to partial decomposition during distillation. It forms a colourless oil, which does not solidify at –15°. The vapour, like that of the preceding compounds, attacks the mucous membranes. It is not affected by a mixture of potassium bichromate and sulphuric acid.

In order to estimate the relative facilities with which the bromine in the lateral chain of these three isomerides can be replaced, Jackson heated in a water-bath three small flasks containing a mixture of 4 grams of each of the three bromides with 2 grams of sodium acetate and 20 c.c. of absolute alcohol. After about half an hour the flasks were allowed to cool, and the amount of sodium bromide which had formed in each was estimated by precipitation with silver nitrate. It was thus found that the amounts of bromine eliminated from 4 grams of the para-, meta-, and ortho-compounds were 0.3927, 0.2834, and 0.0907 grams respectively, which numbers are in the ratio of 1 : 3.179 : 4.329. The square roots of these latter numbers are—

1, 1.783, 2.081.

Now if in a regular hexagon four consecutive angles be distinguished by the letters

a, b, c, d , the lengths of straight lines joining the angles a and b , a and c , and a and d respectively are in the ratio of

$$1 : 1.732 : 2$$

The striking coincidence of these two series of numbers (due allowance being made for unavoidable errors of experiment) may give some support to the hypothesis that the differences in the facility of replacement depend upon the distances between the bromine-atoms in the molecule, and that the amount of replacement increases with the square of this distance.

Benzyl Chloride, $C^6H^5.CH^2Cl$. Reactions. 1. With Water.—When benzyl chloride is heated with water, the first product obtained is the chloride, $C^6H^{10}Cl = C^6H^5.CH^2.C^6H^4.CH^2Cl$, which, by elimination of HCl , may be converted into the hydrocarbon $C^{12}H^{12}$, or, by further action of the benzyl chloride, into the chloride, $C^{12}H^{10}Cl$, which then undergoes similar transformations. By the action of water on these chlorides, the corresponding alcohols and ethers are produced. The crude product, freed by a stream of aqueous vapour from undecomposed benzyl chloride, and then distilled under ordinary pressure, yields chiefly hydrochloric acid, water, benzyl chloride, benzyl-toluene, and resinous or viscid hydrocarbons, which, when further heated, yield anthracene and toluene, together with small quantities of other substances. The anthracene and benzyl-toluene are not contained in the crude product, but are formed during the distillation. When the crude product is distilled in a vacuum, the decomposition of the chloride, $C^{12}H^{10}Cl$, is less energetic, less hydrochloric acid being given off, and large quantities of benzyl chloride, benzyl-toluene, and resinous hydrocarbons being formed. These latter are obtained as masses resembling colophony; they melt below 100° , boil without decomposition in a vacuum, but when heated under ordinary pressure are immediately resolved into anthracene and toluene. The chloride, $C^{12}H^{10}Cl$, boils in a vacuum at 204° – 206° , with partial decomposition, and yields, by distillation under ordinary pressure, benzyl chloride, benzyl-toluene, and a residue which subsequently yields anthracene and toluene. The distillation of the crude product also yields a small quantity of a hydrocarbon boiling, under a pressure of 20 to 30 mm., at 264° – 267° , a solid hydrocarbon melting at a lower temperature, benzoic aldehyde, and anthraquinone. The benzyl-toluene formed in these decompositions yields by oxidation α -benzoyl-benzoic acid, and a small quantity of another acid, probably β -benzoyl-benzoic acid (Weber a. Zincke, *Deut. Chem. Ges. Ber.* vii. 276).

2. With sodium-amalgam.—Benzyl chloride, heated for some time to 100° – 120° with water and sodium-amalgam containing 1 per cent. sodium, gives off hydrochloric acid, and yields a small quantity of stilbene, together with oily products which begin to boil at 300° , and do not contain mercury (Aronheim, *Deut. Chem. Ges. Ber.* viii. 1406).

3. With Methylal. By adding sulphuric acid to a well-cooled mixture of methylal and benzoyl chloride, dichloroglycylmethylphenylmethane, $CH_2(C^6H^4.CH^2Cl)_2$, is obtained, which crystallises from chloroform, methyl alcohol or acetone, in brilliant white plates melting at 106° – 108° (Weiler, *ibid.* vii. 1185). See METHANE-DERIVATIVES and METHYLAL.

4. With Aromatic Hydrocarbons. When benzene and its homologues are heated with benzyl chloride and powdered zinc, a series of hydrocarbons is produced, having the general formula $C^6H^5(C^6H^5)^n$, viz. benzyl-benzene, $C^{12}H^{12}$, benzyl-toluene, $C^{12}H^{14}$, benzyl-xylene, $C^{12}H^{16}$, &c. (2nd Suppl. 182).

In the case of benzene, the higher-boiling portion of the distillate contains two modifications of dibenzyl-benzene, $C^{14}H^{14}(C^6H^5)_2$; toluene similarly treated yields, in addition to monobenzyl-toluene, a quantity of higher-boiling liquid consisting mainly of poly-benzylated toluenes, or allied hydrocarbons, together with smaller quantities of anthracene, and liquid hydrocarbons probably not related to toluene, but formed by decomposition of benzyl chloride (see BENZYL-TOLUENE under DIPHENYL-DERIVATIVES); and naphthalene in like manner yields, together with a large quantity of resin, a thick oily liquid, which, according to Zincke, deposits crystals only after long standing; according to Frôté a. Temmasi, on the other hand, it partly solidifies in the receiver, the solid substance thus obtained consisting of benzyl-naphthalene, $C^{18}H^{18}(C^6H^5)$.

According to Zincke, most aromatic hydrocarbons of high boiling point behave in a similar manner with benzyl chloride and zinc, the benzyl chloride itself, however, being partly decomposed by the heat into hydrogen chloride and resinous products (*Deut. Chem. Ges. Ber.* vi. 137).

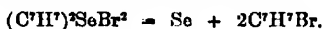
5. With naphthylamine, in presence of a small quantity of zinc powder, benzyl chloride yields benzyl-naphthylamine, $NH(C^6H^4)(C^6H^5)$ (Frôté a. Tor—*Bull. Soc. Chim.* [2], xx. 67). See NAPHTHYLAMINE.

ZYL SELENIDES (C. L. Jackson, *Liebig's Annalen*, clxix. 1; *Deut. Chem. Ges. Ber.* vii. 111, 1277). The monoselenide, or *Selenbenzyl*, $(C^6H^5)_2Se$, is formed by the action of benzyl chloride on a solution of phosphorus pentaselenide in alcoholic soda. The solution when evaporated first deposits the monoselenide in white needles, and afterwards the diselenide in yellow scales.

The monoselenide may be purified by recrystallisation from alcohol or ether, and is thus obtained sometimes in needles, sometimes in broad well-defined prisms, especially when an excess of benzyl chloride has been used in its preparation. It has a faint odour, melts at 45.5° , is insoluble in water, easily soluble in alcohol and ether, and burns with a smoky flame exhibiting the blue colour of selenium. *Platinic chloride*, added to its alcoholic solution, throws down the compound $2(C^6H^5)_2Se.PtCl_4$, as a yellow powder slightly soluble in alcohol, insoluble in water.

Selenbenzyl nitrate is obtained by gently heating the monoselenide with nitric acid as a white mass, which crystallises from alcohol in rhombic prisms melting at 88° , insoluble in water, easily soluble in alcohol, sparingly in ether. The alcoholic solution of this nitrate gives with *hydrochloric acid* a white precipitate of selenbenzyl chloride, which crystallises from alcohol in yellow needles, decomposing below the boiling point of alcohol, with separation of selenium and emission of vapours which have the odour of benzyl chloride. On treating the nitrate with *hydrobromic acid*, selenium is immediately deposited, and vapours are given off which strongly irritate the eyes. The same effects are produced, though less quickly, by bromide of sodium. *Potassium iodide* forms in the solution of the nitrate a yellow precipitate which soon turns brown.

From the reactions just described the chloride and bromide of selenbenzyl appear to decompose in the manner represented by the equation :



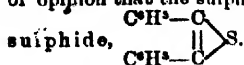
Benzyl diselenide, $(C^6H^5)_2Se_2$, is best prepared by boiling sodium selenide with alcohol and benzyl chloride for several hours in a flask with reversed condenser. It crystallises from alcohol in unctuous yellow scales, which when exposed to sunshine decompose on the surface, and acquire a fine red colour. It is nearly inodorous when pure; melts at 90° , remaining fluid for a long time; burns with a smoky flame, exhibiting the blue colour of selenium; is insoluble in water, easily soluble in hot, less in cold alcohol, still less in ether. When boiled with copper or silver it gives up selenium. It is not acted upon by hydrochloric acid, but is oxidised by nitric acid to benzyl-selenious acid, $C^6H^5.SeO.OH$ (p. 321). With methyl iodide it forms trimethylselenonium iodide, $(CH_3)_3S^+I^-$, and probably benzyl iodide (p. 321).

ZYL SELENIOCYANATE, C^6H^5SeCN , produced by the action of benzyl chloride on potassium seleniocyanate, crystallises in white prismatic needles having a much more repulsive odour than the thiocyanate. It melts at 71.5° , is insoluble in water, but dissolves readily in hot alcohol or ethers.

Nitrobenzyl seleniocyanate, $C^6H^4(NO_2)SeCN$, obtained by treating the preceding compound with cold fuming nitric acid, or by the action of nitrobenzyl chloride on potassium seleniocyanate, forms groups of white needles, melting at 122.5° , and having a less powerful odour than the seleniocyanate of benzyl. It is nearly insoluble in water and in alcohol, but dissolves in aqueous sal-ammoniac (C. L. Jackson, *Deut. Chem. Ges. Ber.* viii. 321).

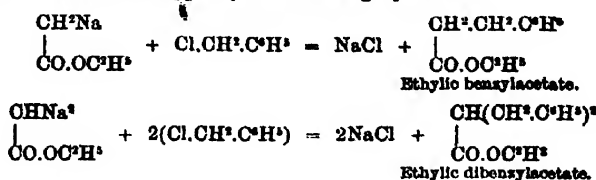
ZYL SULPHIDE, $(C^6H^5)_2S$. According to Märcker (v. 859), this compound crystallises from its solution by slow evaporation in long needles, by rapid cooling in laminae. Forst, on the other hand (*Liebig's Annalen*, clxxviii. 370), finds that it never crystallises in needles, but that it separates from ether or chloroform always in large thick tablets melting at $49^\circ-50^\circ$. According to measurements by C. Bodewig, these crystals belong to the orthorhombic system, having sometimes an elongated, sometimes a very short prismatic development, with much distortion in the latter case. Axial ratio $a : b : c = 0.8126 : 1 : 0.5150$. Combination $\infty P \infty . \infty \bar{P} \infty . \infty P . P$.

According to Barbier (*Compt. rend.* lxxviii. 1772), benzyl sulphide when distilled yields stilbene, $C^{14}H^{12}$, and stilbene sulphide, $C^{14}H^{12}S$. Forst, on the other hand, is of opinion that the sulphur-compound thus obtained was probably impure to allyl-



BENZYL-ACETIC ACIDS (Lydia Sesemann, *Inaugural Dissertation*, Zürich, 1874; *Deut. Chem. Ges. Ber.* vi. 1086). When the yellow solid product obtained by

gradually heating acetic ether with sodium to 160° is mixed with benzyl chloride, and then heated to 200° in a flask fitted with a reversed condenser, ethylic ethers of benzyl-acetic and dibenzyl-acetic acid are formed, the reaction being expressed, according to the views of Frankland & Duppa, by the following equations:—



ETHYLIC BENZYLACETATE, $\text{CH}^2(\text{C}^2\text{H}^2).\text{CO}^2\text{C}^2\text{H}^2$, is a limpid liquid boiling at 245° – 250° and having a fruity smell. The acid contained in it is identical with that described under the names homotolnic, hydrocinnamic, and phenyl-propionic acid.

ETHYLIC DIBENZYLACETATE, $\text{CH}(\text{C}^2\text{H}^2)^2.\text{CO}^2\text{C}^2\text{H}^2$, forms a golden-yellow fragrant oil, which boils above 300° . On saponifying it and decomposing the salt with hydrochloric acid, the free acid is obtained, which crystallises from petroleum-naphtha in quadragic prisms melting at 85° ; it is insoluble in water, but dissolves readily in alcohol and ether. The *barium salt*, $[(\text{C}^2\text{H}^2.\text{CH}^2)^2\text{CH}.\text{CO}^2]\text{Ba}$, is a dense white precipitate, which is insoluble in cold water, sparingly soluble in boiling water, and crystallises from it in fine white needles. The *calcium salt* is a similar precipitate, containing 1 mol. of water, and the *silver salt* forms a flocculent and perfectly insoluble precipitate. An aqueous solution of the ammonium-salt, containing 10 per cent., gave the following characteristic precipitates:—

	In the cold.	On heating.
Ferric chloride	Pale-yellow	Ochre-yellow.
Cobalt nitrate	Reddish-violet.	Dark-violet.
Manganese chloride	White.	Brownish-yellow.
Nickel sulphate	White	Apple-green; on cooling fine needles separate out.
Copper nitrate	Light-blue	Dark-green.

By the action of phosphorus pentachloride on the acid, no chloride, but apparently a substitution-product, was obtained. When barium dibenzylacetate is heated with soda-lime, some benzene is formed, and dibenzylmethane, $\text{CH}^2(\text{CH}^2\text{C}^2\text{H}^2)^2$, an oily liquid boiling above 300° . On adding it in small quantities to warm fuming nitric acid, dinitrodibenzylmethane, $\text{CH}^2(\text{CH}^2\text{C}^2\text{H}^2\text{NO}^2)^2$, is formed, separating from a solution in petroleum naphtha as a pasty mass, which by washing with carbon sulphide, is converted into an amorphous powder melting at 186° .

The formation of the above two acids is quite analogous to Frankland and Duppa's synthesis of butyric and diethylacetic acids, &c. But while these chemists observed at the same time the formation of carboketonic ethers, benzyl chloride does not form similar compounds. This shows that the latter compound, which belongs at the same time to the aromatic and the fatty group, does not behave exactly as the haloïd ethers of the ethyl-series.

BENZYLACETO - ACETATE ETHYLIC, $\text{C}^2\text{H}^2\text{H}^2\text{O}^2 = \text{CH}^2.\text{CO}.\text{CH}(\text{CH}^2\text{C}^2\text{H}^2).\text{CO}.\text{OO}^2\text{H}^2$, is formed by the action of benzyl chloride on ethylic acetosodacetate (p. 13). When decomposed by an alkali, it yields methyl-phenylethyl ketone, $\text{CH}^2.\text{CO}.\text{CH}^2.\text{CH}^2\text{C}^2\text{H}^2$, boiling at 235° (Ehrlich, *Deut. Chem. Ges. Ber.* vii. 892).

BENZYLAMINES, NITRO- and AMIDO- (Strakosch, *Deut. Chem. Ges. Ber.* vi. 1066). The nitro-bases, secondary and tertiary, are formed by the action of ammonia on nitrobenzyl chloride, $\text{C}^2\text{H}^2(\text{NO}^2).\text{Cl}$, and the corresponding amido-bases by treating the nitro-bases with tin and hydrochloric acid. The primary nitro- and amido-bases have not yet been obtained.

Nitrobenzylamines.—To prepare these bases, nitrobenzyl chloride—obtained by gradually adding benzyl chloride to fuming nitric acid cooled to -15° , till the mixture assumes a dark brown colour, pouring this mixture into cold water and crystallising the washed and pressed precipitate from alcohol—is heated to 100° with aqueous ammonia, whereby a brown mass is obtained, which dissolves for the most part in

* It might also be represented according to the views of Wislicenus already explained (pp. 11–12).

hydrochloric acid, yielding the hydrochloride of secondary nitrobenzylamine, $\text{C}^6\text{H}_5\text{NO}_2\cdot\text{CH}_2\text{NH}_2\cdot\text{HCl}$. This salt crystallises in lustrous, yellow prisms, which melt at 212° , and are difficultly soluble in water, alcohol, and hot hydrochloric acid. With platinic chloride it forms a double salt, $(\text{C}^6\text{H}_5\text{NO}_2\cdot\text{CH}_2\text{NH}_2\cdot\text{HCl})_2\text{PtCl}_4$, crystallising in pale yellow needles, almost insoluble in alcohol and in hot water. The free base, obtained by precipitating the hydrochloride with soda, crystallises from alcohol in large shining plates of a yellow colour, melting at 93° , soluble in hot alcohol, but insoluble in water and in ether. It seems to be capable of distilling alone without decomposition, but does not volatilise with vapour of water.

After the secondary nitrobenzylamine has crystallised out from the solution

soluble in alcohol, hot water, and hot hydrochloric acid. The free base likewise crystallises in yellow nodules which are insoluble in water.

The portion of the original product insoluble in hydrochloric acid consists of

tertiary nitrobenzylamine, $\text{C}^6\text{H}_5\text{NO}_2\cdot\text{CH}_2\text{N}(\text{CH}_2\text{C}^6\text{H}_5)_3$, and may be purified by crystallising it, first from nitrobenzene, and subsequently from glacial acetic acid. It forms white lustrous needles, which melt at 163° , and are insoluble in water or in ether, and only very slightly soluble in hot alcohol. It is also formed by digesting secondary nitrobenzylamine with an alcoholic solution of nitrobenzyl chloride at 100° for about four hours.

As the action of ammonia on benzyl chloride yields all three amines, it might be expected that primary nitrobenzylamine would be formed together with the other bases. Such, however, is not the case; neither can this compound be formed from secondary nitrobenzylamine by treatment with hydrochloric acid at a high temperature.

Amidobenzylamines.—Secondary amidobenzylamine is produced when the corresponding nitrobenzylamine is reduced by tin and hydrochloric acid. The hydrochloride, $\text{C}^6\text{H}_5\text{NH}_2\cdot\text{CH}_2\text{NH}_2\cdot\text{HCl}$, obtained by decomposing the stannochloride with sulphuretted hydrogen, crystallises in white lustrous scales, which are insoluble in alcohol and ether, easily soluble in water, less so in hydrochloric acid. The platinochloride, $(\text{C}^6\text{H}_5\text{NH}_2\cdot\text{CH}_2\text{NH}_2\cdot\text{HCl})_2\text{PtCl}_4$, crystallises in large, reddish yellow needles, easily soluble in hot water, but insoluble in alcohol. The free base, precipitated from an aqueous solution of the hydrochloride by soda, crystallises in glistening needles or plates, which melt at 106° , and are soluble in hot water, alcohol, and ether. It may be distilled without decomposition, and becomes coloured by exposure to the air. The sulphate and nitrate form easily soluble needles.

Tertiary Amidobenzylamine, $\text{C}^{12}\text{H}_{17}\text{N} = \text{C}^6\text{H}_5\text{NH}_2\cdot\text{CH}_2\text{N}(\text{CH}_2\text{C}^6\text{H}_5)_2$. The prolonged action of tin and hydrochloric acid on tertiary nitrobenzylamine, cause the tertiary amido-compound at first formed to split up into secondary amidobenzylamine and toluidine; but if the action of the reducing agent be continued only until the nitrobenzylamine has dissolved, and the tin be at once precipitated by sulphuretted hydrogen, a solution is obtained, from which soda precipitates the white crystalline tertiary amidobenzylamine. This base forms brilliant octohedrons, which melt at 136° , and are insoluble in water, but readily soluble in hot alcohol or ether; it distils unchanged. The hydrochloride crystallises in yellow needles, which are exceedingly soluble in water, hydrochloric acid, and alcohol. The platinochloride is an amorphous, yellow compound.

Primary amidobenzylamine does not appear to be formed either by treating nitrobenzyl chloride with ammonia and ammonium sulphide, or by the nitration of acetobenzylamide.

Nitrobenzylphenylamine, $\text{C}^{11}\text{H}_{11}\text{NO}_2 = \text{C}^6\text{H}_5(\text{NO}_2)\cdot\text{CH}_2\text{—NH}(\text{C}^6\text{H}_5)$, is produced by the action of aniline in excess on nitrobenzyl chloride. The product mixed with hydrochloric acid solidifies to a crystalline pulp, from which warm dilute hydrochloric acid extracts hydrochloride of aniline, leaving the hydrochloride of nitrobenzylphenylamine, $\text{C}^{11}\text{H}_{11}\text{NO}_2\cdot\text{HCl}$, undissolved. This salt crystallises from hot concentrated hydrochloric acid in white shining scales, which are soluble in absolute alcohol, but are decomposed by water into hydrochloric acid and the free base. The platinochloride forms brown, shining scales, soluble in water and in hydrochloric acid. The

free base crystallises in golden-yellow needles, which melt at 68° , and are soluble in hot alcohol, ether, and benzene, but insoluble in water.

Amidobenzylphenylamine, $C^{10}H^{10}N^2 = C^6H^5(NH^2).CH^2-NH(C^6H^5)$.—This base cannot be prepared by reduction of the nitro-compound with tin and hydrochloric acid, the reaction proceeding much farther; but by digesting nitrobenzylphenylamine with ammonium sulphide at 100° for a short time, distilling off the excess of sulphide, and repeatedly crystallising the product from concentrated hydrochloric acid, amidobenzylphenylamine hydrochloride, $C^{10}H^{10}N^2.2HCl$, may be obtained in brilliant needles, which are easily soluble in alcohol and in water, less so in hydrochloric acid. The *platinohydrochloride* is dark yellow and amorphous. The *free base* is precipitated by soda from a solution of the hydrochloride, in glistening scales, which melt at 88° , and are readily soluble in ether, alcohol, and benzene.

ACIDS, $C^{10}H^{10}O^2 = C^6H^5.CH^2.C^6H^4.CO^2H$ (Rötering, *loc. cit.*) Two modifications, α and β , are formed by the action of sodium-amalgam on the corresponding benzoyl-benzoic acids. The α -acid, easily produced in this way, is identical with that which is obtained by the action of hydriodic acid on α -benzohydrilbenzoic acid (Zincke, *2nd Suppl.* 177), or on α -benzoyl-benzoic acid (Graebe, *Deut. Chem. Ges. Ber.* viii. 1054). It crystallises from hot water in delicate feathery needles, 2 or 3 c.m. long, melting at 167° . Its *barium salt*, $(C^{10}H^{10}O^2)^2Ba + 2H_2O$, separates from a saturated solution on cooling in small shining moderately soluble laminae. The *calcium salt*, $(C^{10}H^{10}O^2)^2Ca$, crystallises in wavelittic nodules. An *acid calcium salt*, $(C^{10}H^{10}O^2)^2Ca.C^{10}H^{10}O^2$, separates, on passing carbon dioxide into the solution of the neutral salt, as a white precipitate, which dissolves in dilute alcohol, and separates therefrom in fine druses of long thin concentrically-grouped needles.

β -Benzyl-benzoic acid is formed by the prolonged action (8 or 10 days) of sodium-amalgam on β -benzoyl-benzoic acid; if the action be continued for a shorter time only (3 or 4 days), the product consists of β -benzohydril-benzoic anhydride. β -Benzyl-benzoic acid crystallises from alcohol and water in slender shining needles; from hot water in very long broad threads. It melts at 114° , and sublimes in slender needles. It dissolves easily in alcohol, ether, chloroform, and benzene, sparingly in cold, somewhat more easily in boiling water; strong sulphuric acid colours it faintly yellow. The *barium salt*, $(C^{10}H^{10}O^2)^2Ba + 5\frac{1}{2}H_2O$, is moderately soluble in water, and crystallises in concentrically-grouped needles. The *calcium salt* separates from aqueous solution as a flocculent powder, having the composition $(C^{10}H^{10}O^2)^2Ca + 2H_2O$; from dilute alcohol in long shining needles, $[(C^{10}H^{10}O^2)^2Ca + 2C^{10}H^{10}O^2]$. The *silver salt*, $C^{10}H^{10}O^2Ag$, obtained as a white flocculent precipitate on mixing the solution of the ammonium salt with silver nitrate, is nearly insoluble in water, and blackens slowly on exposure to light. The *methyl ether*, $C^{10}H^{10}O^2.CH^3$, obtained by decomposing the silver salt with methyl iodide, is a thick, colorless, non-solidifying liquid, which dissolves easily in alcohol and ether.

BENZYL-DIETHYLSULPHINE IODIDE, $C^6H^5(C^2H^5)_2SI$, is formed, together with other products, by heating 2 mols. ethyl iodide and 3 mols. benzyl sulphide to 100° for several hours; and by agitating the product with silver chloride, filtering, and fractionally precipitating the solution with platinum chloride, the platinohydrochloride of benzyl-diethylsulphine, $[C^6H^5(C^2H^5)_2SI]^2PtCl^4$, is obtained, crystallising in needles (Schöller, *Deut. Chem. Ges. Ber.* vii. 1274).

BENZYL-DIPHENYLAMINE. A name incorrectly given to the compound $C^6H^5 \begin{smallmatrix} \diagup NH.C^6H^5 \\ \diagdown N.C^6H^5 \end{smallmatrix}$ which should be called *benzenyldiphenylamine*. See DIPHENYLAMINE.

BENZYL-ISOPHTHALIC ACID, $C^{12}H^{12}O^4 = C^6H^5.CH^2.C^6H^3(CO^2H)_2$, is formed by treating benzoyl-isophthalic or benzohydril-isophthalic anhydride with sodium-amalgam, the action being continued for six or seven days, and assisted towards the end by heat. The acid separated from the product by hydrochloric acid is purified by conversion into the barium salt, which resembles that of benzoyl-isophthalic acid.

Benzyl-isophthalic acid is a white crystalline powder, nearly insoluble in water, either hot or cold, sparingly soluble in toluene and chloroform, easily in ether, alcohol, and acetone. From hot dilute alcohol it separates in flocks composed of small slender needles, and melting at 242° – 243° . The *barium salt*, $C^{12}H^{12}O^4Ba$, is a white crystalline powder, less soluble in hot than in cold water, and precipitated from its aqueous solution by alcohol. The *calcium salt*, $C^{12}H^{12}O^4Ca + H_2O$, closely resembles the barium salt. The *silver salt* is obtained by precipitation as a white powder. The *ethyl ether*, $C^{12}H^{12}O^4(C^2H^5)_2$, is a thick colourless non-solidifying oil (Blatzbecker).

at the boiling heat. Its *barium salt*, $(C^6H^5O^3)^2Ba + 2H^2O$, forms nodular groups of crystals very soluble in water (Ehrlich, *Deut. Chem. Ges. Ber.* viii. 1208).

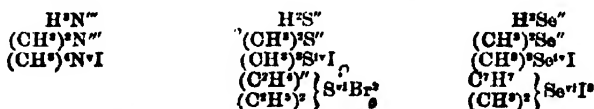
BENZYL-PHENOL, C^6H^5O . See DIPHENYL-DERIVATIVE.

BENZYL-SELENIOUS ACID, $(C^6H^5)SeO^2H$ (C. L. Jackson, *Liebig's Annalen*, clxxix. 13). This acid, analogous to ethyl-selenious acid (1st Suppl. 1015) is produced by gently heating benzyl diselenide with strong nitric acid; the diselenide then dissolves, with evolution of red vapours, to a colourless liquid, which, on cooling, deposits benzyl-selenious acid in crystals, to be purified by recrystallisation from hot water or alcohol, and dried in a vacuum.

This acid crystallises in stellate groups of white needles; when pure it has not a very strong odour, but that of the impure acid is extremely disagreeable. It melts at 85° (uncorr.); dissolves sparingly in cold, very freely in hot water, easily in cold, still more in hot alcohol, but is nearly insoluble in ether. It has a strong acid reaction and decomposes carbonates. Phosphorus pentachloride converts it into a white, stable, crystalline substance not yet examined.

Ammonium Benzyl-selenite is obtained by dissolving the acid in aqueous ammonia, and evaporating over the water-bath, as a white substance which with some difficulty forms crystalline nodules, and is very soluble in water. The *sodium salt*, is a white indistinctly crystalline mass, very soluble in water. The *silver salt* $(C^6H^5)SeO^2Ag$, formed from the ammonium salt by double decomposition, is a white curdy precipitate, and by solution in a very large quantity of boiling water may be obtained as a felted mass of white capillary crystals blackened by exposure to light, but not by the heat of the water-bath. It is very slightly soluble in boiling water, insoluble in cold water, also in alcohol and ether, easily soluble in nitric acid. The *barium salt* is very soluble in water. The *lead salt*, obtained by precipitation, is a white crystalline powder insoluble in cold water, and less soluble in hot water than the silver salt.

BENZYL-SELENONIUM COMPOUNDS (Jackson, *Liebig's Annalen*, clxxix. 16). The term *selenonium* may be applied to selenium compounds containing quadrivalent and sexvalent selenium, analogous in constitution to the ammonium-compounds, containing N^+ , and to the sulphonium-compounds, containing S^+ and S^2+ (commonly, but less appropriately, called sulphine-compounds, v. 881). In fact, the saline compounds containing tetra- and sexvalent sulphur and selenium respectively are derived from the corresponding basal compounds containing bivalent sulphur and selenium, in the same manner as the ammonium salts are derived from the amine-bases, thus:—



Benzyl-dimethylselenonium Tri-iodide, the last compound in the preceding table, is formed, together with trimethylselenonium iodide and benzyl iodide, by digesting benzyl diselenide for several days with excess of methyl iodide. A black mass is thereby formed, which, when treated with water, yields white soluble prisms of trimethylselenonium iodide, and a black residue consisting of benzyl iodide and benzyl-dimethylselenonium tri-iodide:—



The benzyl iodide may be dissolved out by cold alcohol, and the remaining tri-iodide crystallised from boiling alcohol and dried in a vacuum. It then forms black slightly soluble needles, having a metallic lustre and very offensive odour, and melting at 65° (uncorr.) It softens at a few degrees below its melting point, and volatilises to a slight extent below 100° , giving off vapours which strongly attack the eyes. It is insoluble in water, slightly soluble in cold, moderately soluble in hot alcohol and in ether. The red alcoholic solution is decolorised by gentle heating with mercury.

Benzyl-dimethylselenonium Platinochloride, $[(C^6H^5)(CH^3)^2SeCl]^+PtCl_4^-$, is prepared by treating the tri-iodide with alcoholic silver nitrate, mixing the filtered liquid with hydrochloric acid, filtering again, and adding aqueous platinic chloride. The compound then separates after a while as a yellow precipitate consisting of microscopic square crystalline laminae, insoluble in water and in alcohol. When heated it turns brown below 100° , black at a low red heat, and gives off an inflammable vapour.

3rd Sup.

Y

BENZYL-SULPHONIC ACID, $C^6H^5-CH^2-SO^2-OH$. This acid, isomeric with toluenesulphonic acid, $CH^3-C^6H^4-SO^2-OH$, is obtained, as a potassium salt, by boiling benzyl chloride with a moderately strong solution of neutral potassium sulphite (see 2nd Suppl. 184, where the acid is described as *Benzyl-sulphurous acid*).

Benzyl-sulphonic chloride, $C^6H^5.CH^2.SO^2.Cl$, is formed by the action of phosphorus pentachloride on an equal weight of the potassium salt. The action begins at ordinary temperatures, and may be completed with the aid of a gentle heat. The mass, after cooling and washing with water, is dissolved in ether, and on leaving the solution to evaporate, the chloride separates in colourless prisms which melt at 92° , and are resolved at a stronger heat into benzyl chloride and sulphur dioxide. Ammonia converts it into the amide, $C^6H^5.CH^2.SO^2.NH^2$, which forms small prisms moderately soluble in water and melting at 105° (Pechmann, *Deut. Chem. Ges. Ber.* vi. 534).

Dibenzyl-sulphonic Acid, $C^{14}H^{12}(SO^2H)^2 = \begin{matrix} C^6H^5-CH^2-SO^2H \\ | \\ C^6H^5-CH^2-SO^2H \end{matrix}$. This acid is

produced by shaking fused dibenzyl with warm sulphuric acid; on cooling, the liquid solidifies to a magma of crystals, forming, after draining, a light reddish white mass, which, on standing in the air or on addition of a little water, forms a solution from which, on standing, the hydrate, $C^{14}H^{12}(SO^2H)^2 + 5H^2O$, crystallises out in tufts of long needles, whilst by evaporating the solution in a vacuum large plates are formed.

The potassium salt, $C^{14}H^{12}(SO^2K)^2 + 2H^2O$, crystallises in silvery plates. On purifying the crude salt, a small quantity of reddish warty crystals is obtained, consisting of $C^{14}H^{12}(SO^2K)^2 + 3H^2O$.

The barium salt, $C^{14}H^{12}(SO^2)^2Ba + \frac{1}{2}H^2O$, and the lead salt, $C^{14}H^{12}(SO^2)^2Pb + H^2O$, are not insoluble in water, as stated by Fittig & Stelling (*Jahresb. f. Chem.* 1866, 547); they separate from a boiling solution in warty masses.

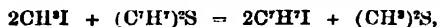
By fusing the potassium salt with potash and adding hydrochloric acid to the solution of the melt, a precipitate is formed, which, after crystallisation from acetic acid, consists of *oxydibenzylsulphonic acid*, $C^{14}H^{12}(OH)(SO^2H)$; and if the fusion with potash be further continued at a high temperature, this last acid is converted into

dioxydibenzyl, $C^{14}H^{10}O^2$, or $\begin{matrix} C^6H^5-CH^2(OH) \\ | \\ C^6H^5-CH^2(OH) \end{matrix}$, which crystallises in white, shining

laminæ, nearly insoluble in cold, moderately soluble in hot water. When purified by sublimation, it melts at 185° .

Simultaneously with the dioxydibenzyl, *para*-oxybenzoic acid is also formed (together with a small quantity of phenol and traces of benzoic acid); and on treating the fused mass with an acid, the *para*-oxybenzoic acid dissolves, while the dioxydibenzyl separates out (R. Kude, *Deut. Chem. Ges. Ber.* vi. 953).

BENZYL-SULPHONIUM COMPOUNDS (C. Schöler, *Deut. Chem. Ges. Ber.* vii. 1274). *Benzyl-dimethylsulphonium iodide*, $(C^6H^5)(CH^3)^2SI$, is formed, together with trimethylsulphonium iodide, $(CH^3)^3SI$, by the action of methyl iodide on benzyl sulphide, either at ordinary temperatures or at 100° in sealed tubes. The first products of the reaction are benzyl iodide and methyl sulphide:—



and the methyl sulphide then enters into combination, partly with benzyl iodide, partly with methyl iodide, forming the two compounds above mentioned. By agitating the product with water, filtering through a wet filter—on which an oily mass remains—and agitating the filtered solution of the iodides with silver chloride, they are converted into the corresponding chlorides; and the solution of these compounds, mixed with platonic chloride and fractionally crystallised, yields at first long orange-red prisms of the tri-*benzyl*-dimethylsulphonium chloride, $(C^6H^5)_3(CH^3)_2S.Cl$, and then orange-red prisms of the tri-*benzyl*-dimethylsulphonium iodide, $(C^6H^5)_3(CH^3)_2S.I$.

Ethyl iodide does not act on benzyl sulphide in the same manner as methyl iodide, at ordinary temperatures; but at 100° in sealed tubes, benzyl-diethylsulphonium iodide is formed, which, by treatment as above, yields a platinum salt having the composition $[(C^6H^5)(C^2H^5)^2SCl]_2PtCl_4$.

BENZYL-TOLUENE, $C^{14}H^{14}$ } See DIPHENYL-DERIVATIVES.
 CH^3

The kernel of the Brazil chestnut (*Bertholletia excelsa*) has been analysed by Corenwinder (*J. Pharm. Chim.* [4], xviii. 14), whose results are

given in the following table, together with those of the analysis of the earth-
(*Arachis hypogaea*).

	Kernel of Brazil chestnut.	Kernel of earth-nut.
Water	8.00	6.76
Oil	65.60	51.75
Nitrogenous substances	15.31	21.80
Organic matter, not nitrogenous	7.39	17.66
Phosphoric acid	1.35	0.64
Lime, potash, silica, &c.	2.35	1.39

100.00

100.00

The percentage of nitrogen in the kernel of the Brazil chestnut is 2.45.

BERYL. C. Gréville Williams (*Proc. Roy. Soc.* xxi. 409) has determined the specific gravity of beryl and of emerald, before and after fusion, with the following results:—

	Beryl.	Emerald.
Before fusion	2.65 to 2.66	2.69 to 2.70
After	2.41	2.40

Artificial beryls, composed exactly according to the analysis of the natural mineral, had a sp. gr. of 2.42.

The green colour of the emerald is due to chromic oxide, not, as sometimes supposed, to carbon compounds. Carbon and hydrogen are indeed present in beryl and emeralds (a beryl gave 0.08 p. c. carbon and 0.06 to 0.11 p. c. hydrogen), but they have nothing to do with the colour. Williams's experiments confirm, indeed, the results obtained long ago by Vauquelin, Klaproth, and Hofmeister (ii. 486), and in 1869 by Boussingault (*Compt. rend.* lxi. 1249).

Websky (*Jahrb. f. Min.* 1876, 774) has examined crystals of beryl from Eidsvold in Norway. They were imbedded in felspar, quartz, or mica; had an emerald-green colour, and exhibited the twelve-sided pyramid, $\frac{1}{2}P\frac{1}{2}$, in addition to ∞P , $0P$, $2P2$, and P .

BETAINES, $C^4H^9NO_2$. *Occurrence.*—This base exists in mangel-wurzel as well as in the sugar beet (Schulze & Urich, *Landw. Versuchs. St.*, xviii. 400). Husemann (*Arch. Pharm.* [2], vi. 216) finds that lycine, the base discovered in 1864 by himself and Marmé in *Lycium barbarum* (iii. 738) is identical with betaine.

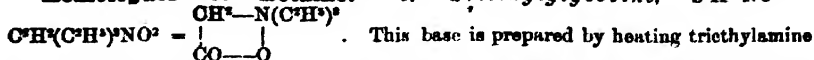
Synthesis.—Betaine has the constitution of trimethyl-glycocine, $C^4H^9(CH^3)_3NO_2$, $CH^3-N(CH^3)_3$



, and should therefore be formed by the action of methyl iodide on glycocine (amidacetic acid), just as trimethyl-amidobenzoic acid (betaine) is produced from amidobenzoic acid (2nd Suppl. 187), and this synthesis has actually been effected by Griess (*Deut. Chem. Ges. Ber.* vii. 1406). One mol. of glycocine, dissolved in excess of strong potash-ley, is mixed with 3 mols. methyl iodide, and then with a quantity of methyl alcohol sufficient to form a uniform mixture. This, when left to itself, soon becomes warm and its alkaline reaction gradually changes to a decided acid reaction. The liquid must then be again rendered alkaline by addition of potash, and this treatment repeated till the alkaline reaction is no longer destroyed even after a further addition of methyl iodide.

The betaine formed by this reaction may be separated (in case only small quantities are operated upon) by neutralising with hydriodic acid, removing the methyl alcohol by distillation in the water-bath, diluting the residue with a little water, and then adding a solution of iodine in hydriodic acid, whereby a periodide of betaine is precipitated in black-brown shining needles, which, after separation from the mother-liquor, may be purified by repeated washing with water. This periodide, suspended in water and treated with hydrogen sulphide, is converted into betaine hydriodide, from which the base and its other compounds may be obtained by known methods.

Homologues of Betaine.



with ethylic chloracetate, boiling the crude product with baryta-water to remove hydrochloride of triethylamine, and treating the resulting chloride of triethylamidacetic acid, $N(CH^3)_3Cl-CH^3-CO^2H$, with silver oxide. Triethylglycocine thus obtained unites both with acids and with bases. It begins to boil at 210° , but only a part of it goes over unaltered, the remainder being resolved into triethylamine and carbonaceous products. The chloride of triethylamidacetic acid just mentioned may

be heated with strong bases to a somewhat high temperature without undergoing decomposition (J. W. Brühl, *Deut. Chem. Ges. Ber.* viii. 1408).

2. *Trimethyl- α -propiobetaine*, $C^6H^{13}NO^2 = \begin{array}{c} CH_3-CH-N(CH_3)_2 \\ | \\ CO-O \end{array}$, is formed

by the action of ethylic α -chloropropionate on trimethylamine. The action begins at ordinary temperatures, and may be completed by heating the materials together for twelve hours in sealed tubes in a water-bath: it takes place most readily in alcoholic solution. The product, consisting of the hydrochlorides of trimethylamine and trimethyl- α -propiobetaine, may be freed from trimethylamine by boiling with baryta-water; and, on removing the baryta with sulphuric acid, the latter by lead hydrate, and leaving the filtered solution to evaporate over sulphuric acid, it solidifies to a mass of extremely deliquescent apparently cubical crystals of trimethyl- α -propiobetaine.

This base has a neutral reaction, no smell, but an aromatic and very sweet taste; dissolves easily in alcohol, but is insoluble in ether. It begins to boil at 210° , giving off large quantities of trimethylamine, together with a small quantity of a brownish empyreumatic oil. It unites readily with acids, forming very hygroscopic salts. The *platinochloride*, $C^6H^{13}NO^2.HCl.PtCl^4$, separates as an orange-coloured pulverulent precipitate on adding hydrochloric acid and platinic chloride to an alcoholic solution of the betaine, and crystallises from water in large shining roseate prisms with pointed end-faces; it is insoluble in ether. The *aurochloride*, $C^6H^{13}NO^2.HCl.AuCl^3$, crystallises in long needles having a golden lustre; dissolves easily in hot water, alcohol, and ether, but is insoluble in chloroform. The *iodide*, $C^6H^{13}NO^2.C^2H^5I$, forms colourless shining prisms, several centimeters long, permanent only when quite pure. It is very soluble in alcohol and in hot water, only slightly soluble in cold water, insoluble in ether (Brühl, *Deut. Chem. Ges. Ber.* 1876, p. 34).

ANAL. O. Jacobsen (*Deut. Chem. Ges. Ber.* vi. 1026) has made an examination of bile taken from a healthy man, through a biliary fistula which remained open for several weeks. This bile was a clear neutral liquid having a greenish brown-yellow colour. The sp. gr. varied from 1.0105 to 1.0107; the amount of solid constituents from 2.24 to 2.28 per cent. Albuminoids and leucine were present only in the first few days after the opening of the fistula; sugar and urea were absent; the only bile-pigments found were bilirubin and biliverdin. The composition of the ash was as follows:—

	KCl	NaCl	CO ² Na ⁺	PO ³ Na ⁺	(PO ³) ² Ca
In per cent. of ash	3.30	65.16	11.11	15.90	4.44 = 100
In per cent. of dry bile	1.276	24.508	4.180	5.984	1.672 = 37.620

The ash also contained small quantities of iron, silica, magnesia, and traces of copper.

The dry residue of the bile contained the following amounts of organic substances:—

Cholesterin	2.49 per cent.
Unsaponified fats and a little oleate of sodium	0.44 "
	0.21 "
Glycocholate of sodium	44.80 "
Palmitate and stearate of sodium	6.40 "
Organic substances insoluble in ether and in alcohol	10.00 "

Taurocholic acid was not present in this bile; but the examination of specimens of bile from patients who had died of various diseases showed that this acid does also occur in human bile, and that its proportion to glycocholic acid varies within very wide limits.

The distillate of putrid bile has been found to contain trimethylamine, the formation of which is due to the putrefactive decomposition of the neurine of the bile. Addition of considerable quantities of neurine to the bile prevents the putrefaction (J. Mauthner, *Liebig's Annalen*, clxvi. 202).

Action of Peptones.—The precipitate formed by bile in peptone-solutions redissolves in an excess of bile amounting to four or five times the volume of the liquid, the result being but little influenced by the concentration of the peptone-solution. The mycin of the bile does not appear to be concerned in the redissolution of the precipitate. An 8-per cent. solution of crystallised ox-bile also produces in peptone-solutions a precipitate which redissolves in excess of the bile. Dog's bile appears to be less efficacious in redissolving the precipitate (Moleschott, *Chem. Centr.* 1876, 368).

BILE-PIGMENTS. Bilirubin and biliverdin have been variously formulated as follows (1st Suppl. 344):—

	Thudichum.	Städeler.	Maly.
Bilirubin	$C^{10}H^8N^2O^2$	$C^{10}H^{10}N^2O^2$	$C^{10}H^{10}N^2O^2$
Biliverdin	$C^8H^8N^2O^2$	$C^{10}H^{10}N^2O^2$	$C^{10}H^{10}N^2O^2$

Maly (*Liebig's Annalen*, clxxv. 76) recommends the preparation of bilirubin from the gall-stones of oxen, which contain 28.10 per cent. of that substance. By the analysis of biliverdin and the determination of the quantity of it obtainable from a given weight of bilirubin, he considers that his formula above given for that substance is confirmed.

Bromo-bilirubins (Thudichum, *Chem. Soc. Jour.* 1876, 389; 1876, ii. 27; Maly, *Liebig's Annalen*, clxxi. 106).—Thudichum finds that bilirubin, treated for a short time with bromine-vapour and heated to 100° till no more hydrobromic acid is given off, yields monobromobilirubin, $C^8H^8BrN^2O^2$, soluble in concentrated hydrochloric, hydrobromic, and sulphuric acids. By prolonged action of the bromine-vapour, dibromobilirubin, $C^8H^8Br^2N^2O^2$, is formed, which dissolves in alcohol with violet-colour, in glacial acetic acid and in strong sulphuric acid with purple colour.

According to Maly, tribromobilirubin has the composition $C^8H^8Br^3N^2O^2$. He prepares it by triturating bilirubin with chloroform free from alcohol, and adding to the liquid a dilute solution of bromine in chloroform till a dark mass settles on the sides of the vessel. By decanting the chloroform, washing the remaining dark mass with hydrobromic acid, then dissolving it in alcohol, and precipitating with water, the bromine-compound is obtained in the form of a dark blue-green powder which dissolves in alcohol with deep-blue colour. Maly regards the composition of tribromobilirubin as a proof that the usually received formula of bilirubin, $C^8H^8N^2O^2$, should be doubled. He represents the formation of tribromobilirubin by the equation—

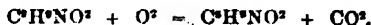


and finds that this equation is confirmed by the increase in weight of a known quantity of bilirubin when treated with bromine.*

Tribromobilirubin is insoluble in water, but dissolves easily in alcohol and ether; it likewise dissolves in alkalis, but is decomposed by the action of strong alkaline liquids, and converted into biliverdin. Sodium-amalgam converts it into hydro-bilirubin. Hydrogen sulphide and ammonium sulphide change the blue colour of a solution of tribromobilirubin to green; nitric acid, aided by gentle heat, turns it to dark red, and afterwards to brown-yellow (Maly).

Chlorobilirubins.—Dry bilirubin is immediately bleached by dry chlorine. A solution of bilirubin in chloroform, treated with chlorine at 16°, yields trichloro-bilirubin, $C^8H^8Cl^3N^2O^2$; at 100° tetrachloro-, and perhaps also pentachlorobilirubin (Thudichum, *Chem. Soc. Jour.* 1876, 389).

Bromobiliverdin is obtained by the action of bromine-vapour on biliverdin, as a black powder insoluble in ether, slightly soluble in alcohol, easily soluble in soda-ley, from which it is precipitated by acetic acid. Its composition is $C^8H^8BrN^2O^2$, according to analyses by Thudichum, who regards this result as a further confirmation of his view that bilirubin is converted into biliverdin in the manner represented by the equation:—



The reduction of an alkaline solution of biliverdin by sodium-amalgam yields hydrobiliverdin, the alcoholic solution of which exhibits an absorption-spectrum different from that of hydrobilirubin (Thudichum, *Chem. Soc. Jour.* 1876, ii. 27).

Bilifuscin, originally described by Bücke (1st Suppl. 344), has been further examined by A. Simony (*Wien. Acad. Ber.* [3 Abth.], lxxiii. 181). Bile from a corpse, after exhaustion with chloroform, was diluted with water and acidulated with acetic acid; the separated mucus, which carried down with it the greater part of the colouring matter, was washed with water and then exhausted with alcohol; and the residue left after evaporation of the alcohol was well boiled with water to remove biliary acids, then dissolved in a little alcohol, and precipitated with ether.

Bilifuscin thus prepared does not give Gmelin's reaction.† It dissolves easily in alcohol, glacial acetic acid, and alkalis, with brown colour verging on olive-green; sparingly in chloroform; but is insoluble in water, ether, and dilute acids. The alcoholic solution exhibits a uniform darkening of the violet and indigo-blue part of the spectrum. Bilifuscin, heated with zinc-dust, yields a distillate which reddens a deal shaving moistened with hydrochloric acid, and gives a brick-red precipitate

* These results are contested by Thudichum, who likewise objects to the statements of Maly and of Heymans. A. Campbell respecting the oxidation of bilirubin by bromine-water, also to those of Maly on hydrobilirubin, and of Jaffé on urobilin (2nd Suppl. pp. 189, 190).

† Change of colour from green to blue, violet, red, and finally yellow, produced on addition of nitric or nitrous acid (Gmelin's Handbook, English Edition, xviii. 70).

with fuming nitric acid. Bilifuscin does not reduce an ammoniacal solution of silver nitrate. Dissolved in glacial acetic acid and boiled with peroxide of lead, it yields a yellow substance soluble in chloroform. When bilifuscin is boiled with baryta-water, the liquid evaporated, the residue exhausted with glacial acetic and hydrochloric acids, and the resulting solution shaken up with chloroform, a colouring matter is obtained which exhibits an absorption-band in the spectrum between E and F, but is different from urobilin.

BILIARY ACIDS. *Cholic acid*, $C^{24}H^{40}O^5$. H. Tappeiner (*Deut. Chem. Ges. Ber.* vi. 1285) obtains ethylic cholate, crystallised and exhibiting all the properties described by Hoppe Seyler (*J. pr. Chem.* lxxxix. 272), by leaving an alcoholic solution of cholic acid, saturated with hydrochloric acid, at rest for three or four hours, then diluting it with water and adding sodium carbonate. A resinous mass (not yet examined) then separates on the surface, while the cholic ether separates in the crystalline form, and may easily be purified by recrystallisation from alcohol.

Cholic acid, oxidised with potassium chromate and sulphuric acid, yields, together with acetic acid, two well-crystallised acids, one which is either palmitic or stearic acid, or a mixture of the two;—while the other is but slightly soluble in water; crystallises from alcohol in needles; may be heated without alteration to 200° ; but melts with decomposition at a higher temperature (Tappeiner).

Glycocholic acid.—For preparing this acid in the pure state, the following process is recommended by G. Hüfner (*J. pr. Chem.* [2], x. 267). Fresh bile contained in a tall cylinder is covered with a layer of ether, and pure strong hydrochloric acid is added in the proportion of 2 c.c. to every 50 c.c. of the bile; the crystalline pulp, which forms after some time, is left to drain on a filter, and the impure crystals of glycocholic acid thus obtained are recrystallised from hot water.

When nitrous acid vapour is passed through a solution of glycocholic acid in nitric acid, an acid called chologlycocholic acid is formed, having the composition $C^{26}H^{42}O^7$. This acid may be separated by supersaturating the liquid with baryta, removing the excess of baryta with carbonic acid, and treating the filtered solution with hydrochloric acid. It has not been obtained in the crystalline state. When boiled with dilute hydrochloric acid, it yields glycocholic acid (J. Lang, *Bull. Soc. Chim.* [2], xxv. 180).

Glycodyslysin, $C^{26}H^{42}NO^4$.—This compound is formed by heating cholic acid with glycocine in a sealed tube to 190° – 200° for twelve to twenty-four hours, whereby a fused mass is obtained which dissolves almost completely in absolute alcohol. On adding water to this solution, a milky liquid is obtained, which becomes clear in a few days, and when mixed with soda-ley yields glycodyslysin as an amorphous precipitate easily soluble in methyl alcohol, ether, and chloroform. The same substance appears to be formed by heating glycocholic acid to 190° – 200° . It is a perfectly indifferent body, and when boiled with alcoholic potash does not yield either cholic or glycocholic acid; but when boiled for a long time with hydrochloric acid it yields glycocine (Lang, *loc. cit.*)

BINNITE. Crystals of this mineral from the Binnenthal exhibit the following forms.

- (1). $\infty O \infty . O . \infty O$.
- (2). $\infty O \infty : \infty O$, of the true character of tin-stone.
- (3). $\infty O \infty . \infty O . O . 2O2 . 3O\frac{1}{2}$.
- (4). $\infty O \infty . \infty O . 2O2 . \frac{3}{2}O\frac{1}{2}$.
- (5). $\infty O \infty . \infty O . O . 2O2 . 6O6$.

(A. Schrauf, *Jahrbuch für Mineralogie*, 1874, p. 960.)

BISMUTH. *Occurrence*.—Bismuth and several of its compounds have, lately been found in considerable quantities at Meymac in the department of the Corrèze, France (Carnot, *Compt. rend.* lxxix. 302, 477); also in the district of Colorado, U.S. (Burkart, *Jahrbuch f. Mineralogie*, 1874, 29); and in Utah (Burkart, *ibid.* 310).

Native Bismuth occurs at Meymac in irregular, brittle, white, lamellated nodules, having a crystalline fracture, and becoming red on exposure to the air: composition—

Bi.	Pb.	Fe.	Sb.	As.	S.
99.00	0.41	0.10	0.15	0.09	0.06 = 99.81.

Bismuth Carbonate, or *Bismutite*, is imported from Mexico (locality not exactly known) in large quantities, and in a tolerably pure state. It forms greyish-white, turbid, crystalline, or compact lumps, from the size of a pea to that of a hazel-nut, frequently also pseudomorphs after scheelite, not hitherto observed. These pseudomorphous crystals are either pyramidal or tabular; the tabular crystals are commonly united in rosette-shaped or spherulic groups, and indistinctly developed, whereas the pyramidal crystals are for the most part very well defined, with sharp edges and even faces. The pyramid P and the dome $2P\infty$ occur independently, the latter being the

more frequent. The most ordinary combinations are $2P_{\infty} \cdot oP$ and $P \cdot oP$. The tabular crystals exhibit the faces, oP , $\frac{1}{2}P$, as well as ∞P .

This bismutite gave by analysis—

Bi_2O_3 .	CO_2 .	SO_2 .	H_2O .	Residue.
30.10	7.00	0.27	1.80	0.30 = 99.47

(Frenzel, *Jahrbuch f. Mineralogie*, 1873, 785.)

A basic hydrocarbonate, probably $2Bi_2O_3 \cdot Bi_2O_3 \cdot (H_2O \cdot CO_2)$, occurs at Meymac, generally surrounding native bismuth, and adhering to it. Sp. gr. 9.22. Opaque. Semi-vitreous. Fracture conchoidal. Brittle. Easily pulverised. Colour yellowish green. Soluble in hydrochloric acid with effervescence. Before the blowpipe on charcoal it easily yields a metallic button. It contains 96.70 per cent. of bismuth oxide, with small quantities of the oxides of the metals which accompany the native bismuth in the same locality, and 0.68 per cent. of carbonic acid (Carnot).

Bismuth Trisulphide or *Bismuthinite*, Bi_2S_3 , occurs at Meymac in crystalline masses resembling native antimony sulphide. Sp. gr. = 6.60: composition—

Bi.	S.	Pb.	Cu.	Fe.	Sb.	As.	Gangue.
78.40	14.25	0.75	0.40	0.53	0.85	3.10	0.30 = 99.18

The same mineral occurs in southern Utah mixed with oxide and hydrocarbonate, the last two species being doubtless formed by the alteration of the sulphide (Silliman, *Am. J. of Sci.* [3], vi. 126).

Bismuthic Mispickel occurs at Meymac in crystalline masses, closely resembling ordinary mispickel; the white fracture sometimes becomes slightly red. Composition: I, a mass of crystalline texture; II, a fragment having crystalline faces.

	Fe.	Bi.	Pb.	Cu.	Sb.	As.	S.	Gangue.	Water and loss.
I.	31.90	1.62	0.10	0.16	1.70	40.15	16.34	6.10	1.93 = 100
II.	28.71	6.58	0.10	1.07	1.50	39.30	14.60	5.70	2.44 = 100

Cobalt may easily be detected by the blowpipe. In bulk, the mineral yielded 8 grams of silver per 100 kils., and a quantity of gold too small for estimation. It may be regarded as a mixture of bismuthic mispickel having some of the iron replaced by bismuth and cobalt, with true mispickel.

Telluric Bismuth.—Specimens of this mineral were lately sent to the Royal Mineral Cabinet of Freiberg, from Ormicza in the Banat, where it occurs in laminar or granulo-laminar groups, imbedded in calc spar, and accompanied by zinc-blende and a metallic steel-grey mineral, probably fahl-ore. It exhibits a strong metallic lustre on the very perfect basic cleavage-face.

Its chemical composition (after deduction of an insoluble silicate) was found to be 66.23 p.c. Bi., 25.92 Te, and 4.26 S, agreeing with that of the telluric bismuth of Schubkau, near Schemnitz.

The bismuth and tellurium were separated by precipitating them as sulphides, and treating the precipitate with hydrogen sulphide, which dissolves only the tellurium. The separation cannot well be effected by precipitating the bismuth as basic chloride, inasmuch as the precipitate always carries tellurium down with it, neither can it be effected by precipitating the tellurium with sulphurous acid, since a small quantity of bismuth is always thrown down at the same time (Frenzel, *Jahrb. f. Min.* 1874, 786).

Preparation of pure Bismuth.—1. To obtain Bismuth free from arsenic and sulphur. The metal is heated considerably above its melting point in a vessel which exposes a large surface to the air, so that about a fourth of it may be oxidised, the oxide being thrown to the sides of the vessel as fast as it is formed. The mass when cold is pulverised, mixed with charcoal, dried soap, and potassium carbonate free from sulphate (about a fourth of the weight of the original metal); and the mixture is introduced into a crucible of which it fills about five-sixths, then covered with charcoal, and heated to redness for an hour. The metal thus obtained contains potassium, becomes moist when exposed to the air, and when thrown into water, especially hot water, eliminates a large quantity of hydrogen. To free it from this impurity it is once more fused in contact with the air, whereby the potassium is converted into oxide, which separates as a white film on the surface of the molten bismuth (Méhu, *Pharm. J. Trans.* [3], iv. 341).

2. *Separation of Iron.*—Bismuth absolutely free from iron may be prepared without loss by fusing the ordinary metal under a layer of potassium chlorate mixed with 2 to 5 per cent. of sodium carbonate (H. Türsch, *J. pr. Chem.* [2], xiv. 309).

The separation of bismuth and iron in the wet way is best effected by precipitation with oxalic acid, which throws down from slightly acid solutions a white crystalline precipitate of bismuth oxalate, which is perfectly free from iron, provided it is not

left too long in contact with the liquid or digested on the water-bath. The oxalate is resolved by ignition into carbon dioxide and metallic bismuth (Türach).

3. *Separation of Silver.*—Small quantities of silver cannot be removed from bismuth by precipitation with hydrochloric acid. The only way of effecting the separation is to oxidise the bismuth and leave the silver in the metallic state (Türach).

4. *Separation of Lead.*—According to A. Vogel (*N. Rep. Pharm.* xxii. 474) this separation is best effected by precipitating the lead with excess of sulphuric acid. The whole is then evaporated to dryness, the residue drenched with sulphuric acid, and after the action of this acid has gone on for several hours, the liquid is diluted with water and filtered, and the residue is washed with sulphuric acid.

Volumetric Estimation.—Buisson a. Ferray (*Moniteur scientifique* [3], iii. 900), describe a method founded on the complete precipitability of bismuth in acetic acid solution by iodic acid, as neutral bismuth iodate, $\text{Bi}(\text{IO}_3)_3$. Basic bismuth nitrate (the compound to which the method is most frequently applied) is first dissolved in a few drops of nitric acid; the solution is carefully diluted with water and mixed with sodium carbonate till a slight permanent precipitate is formed; this precipitate is dissolved in excess of acetic acid; the solution is mixed with excess of a titrated solution of iodic acid (30 grams of crystallised iodic acid to 1 litre of water); and the whole, after dilution to 250 c.c. and brisk agitation, is filtered through a dry filter. The excess of iodic acid is then estimated in 100 c.c. of the clear filtrate, by liberating the iodine with dilute sulphuric acid and solution of potassium iodide, and titrating with sodium thiosulphate. The difference between the quantity of iodic acid actually added, and that which remains unaltered after the precipitation, gives the quantity of bismuth iodate produced, whence also the amount of bismuth may be easily calculated. Oxychloride of bismuth, being insoluble in acetic acid, cannot be determined in this manner: hence also the reagents employed in the process above described must be free from chlorine. If the basic nitrate of bismuth is adulterated with lead and barium salts, these must first be removed by a sulphate. Tin and anti-mony compounds are eliminated in the previous treatment with nitric acid.

Muir (*Chem. Soc. Jour.* 1876, i. 483; 1877, ii. 674; 1878, i. 70) has given four methods for the volumetric estimation of bismuth:

(1). A nearly neutral solution of bismuth nitrate is precipitated by *potassium chromate* or *dichromate*, and the critical point is ascertained by testing the clear solution from time to time with silver nitrate till red silver chromate is produced, the strength of the chromium solution having been previously determined by means of a bismuth-solution of known strength. Chlorine, sulphuric acid, calcium, copper, and arsenic interfere seriously with the results of this method, and must therefore be removed before the titration is commenced.

The second and third processes are based on the fact observed by Chancel, that bismuth is precipitated in the form of phosphate by adding a soluble *phosphate* to a solution of the metal in nitric acid.

(2). The bismuth is thrown down from a nitric acid solution, after partial neutralisation with ammonia, by addition of standard solution of sodium phosphate, the final point of the reaction being ascertained by spotting the supernatant liquid on a slab with a warm solution of ammonium molybdate. The results are approximately accurate.

(3). The nitric acid solution of bismuth is mixed with excess of sodium acetate; a measured volume-excess of standardised sodium phosphate is added; the liquid is boiled and filtered; the precipitate is washed with hot water; and the excess of phosphoric acid is determined in the filtrate with a standard solution of uranium acetate. This method gives very exact results, and is much to be preferred to either of the two previously described.

(4). This method is based on the fact observed by Souchay a. Lenssen, that normal bismuth oxalate, when boiled with water, splits up into oxalic acid and a basic oxalate, $\text{Bi}^2\text{O}_3 \cdot 2\text{C}^2\text{O}_3 + \text{H}_2\text{O}$ (iv. 253). An excess of saturated solution of oxalic acid is added to the bismuth solution, the precipitate allowed to settle, the supernatant liquid poured off, and the precipitate boiled with water until free from acid. The residue is now dissolved in dilute hydrochloric acid and titrated with permanganate. The absence of free hydrochloric acid must be ensured before precipitating. The results are accurate, and the method is generally applicable.

Bromides (Muir, *Chem. Soc. J.* 1876, i. 144). The tribromide, BiBr_3 , is most easily prepared by allowing bromine to flow, in successive small quantities, on powdered bismuth contained in a retort with the beak tilted upwards. Much heat is evolved during the reaction: when the mass has become cold, a very low flame is placed at a considerable distance beneath the retort; the heat is maintained and gradually increased during several days, when large, flat, brilliant, golden-yellow

crystals form in the upper part of the retort, at a distance of an inch or so above the heated mass. The same compound is formed by passing carbon dioxide, saturated with bromine vapour, over heated bismuth; but the process above described yields it in greater quantity and with less expenditure of bromine. Bismuth tribromide melts at 210° – 215° .

Bismuth tribromide, gently heated in a current of hydrogen, melts to a dark red liquid, which partially sublimes on the colder part of the tube in yellow crystals, and is partly reduced to metallic bismuth.

The tribromide is instantly decomposed by water, yielding the oxybromide, BiOBr , in the form of a white loose amorphous powder, insoluble in water, unaltered at a red heat, converted into the tribromide by heating with charcoal in a stream of dry chlorine.

Dibromide, Bi^2Br^4 .—In the preparation of the tribromide, dark grey crystalline scales are generally produced, mixed with the yellow crystals. When separated from the latter as completely as possible, they give by analysis 44.37 per cent. bromine, the formula of the dibromide requiring 43.24. By continued heating, these dark grey crystals are gradually resolved into the tribromide and metallic bismuth, the decomposition taking place at a temperature much lower than that of the corresponding dichloride (Muir). Macivor (*Chem. News*. xxx. 190), by heating finely-powdered bismuth with bromine, obtained a dark grey solid (probably also the dibromide), melting at 198° – 200° to a dark red liquid, and boiling at a heat below redness. It is described as insoluble in carbon sulphide, alcohol, and ether, dissolved by hydrochloric acid, decomposed by nitric acid, also by water with formation of an oxybromide.

Ammonio-bromides.—These compounds are formed by the action of ammonia gas on the tribromide and oxybromides of bismuth (Muir, *Chem. Soc. J.* 1876, i. 147; 1877, i. 27).

(a.) Bismuth tribromide heated in a stream of dry ammonia gas yields chiefly three products: (1.) $\text{BiBr}^3 \cdot 3\text{NH}^3$, in the form of a volatile, straw-yellow powder, soluble in hydrochloric acid, and forming a solution, which, when evaporated over sulphuric acid, deposits light yellow, deliquescent, tabular crystals of the compound $\text{BiBr}^3 \cdot 3\text{NH}^3\text{Cl} + \text{H}^2\text{O}$, which is immediately decomposed by water. (2.) An olive-green solid mass, difficult to separate from the sides of the tube, deliquescent, and decomposed by water. Its composition has not been exactly ascertained, on account of the difficulty of obtaining it pure, but is most probably represented by the formula $\text{BiBr}^3 \cdot 2\text{NH}^3$. Its hydrochloric acid solution yields by slow evaporation crystals having the composition $\text{BiBr}^3 \cdot 2\text{NH}^3\text{Cl} + 3\text{H}^2\text{O}$, analogous to that of the double chloride, $\text{BiCl}^3 \cdot 2\text{NH}^3\text{Cl}$, described by Déhérain, and to that of the double bromide, $\text{BiBr}^3 \cdot 2\text{NH}^3\text{Br} + 5\text{H}^2\text{O}$, described by Niklès (*1st Suppl.* 347). (3.) An ash-grey, crystalline, infusible, and non-volatile substance, not decomposed by water or alkalis, but giving off ammonia when heated with soda-lime. The quantity obtained was too small for an exact determination of its composition, but it appears to agree most nearly with the formula, $\text{Bi}^2\text{N}^2\text{Br}$.

(b.) Another ammonio-bromide, $2\text{BiBr}^3 \cdot 5\text{N}^3\text{J}^3$, is formed when the oxybromide, $\text{Bi}^2\text{Br}^3\text{O}^{12}$, is heated to dull redness in a stream of dry ammonia gas, and condenses in the colder part of the tube in the form of a greyish-green powder, while metallic bismuth remains in the form of semi-fused globules. The same oxybromide is obtained, though in smaller quantity, by the action of ammonia gas on heated bismuthyl bromide, BiOBr . It is non-deliquescent, and is not decomposed by water, dissolves readily in dilute acids, and is decomposed by nitric acid with evolution of bromine. When heated it gives off fumes of bismuth tribromide and is almost wholly volatilised, leaving only a small residue, apparently consisting of the oxybromide, $\text{Bi}^2\text{Br}^3\text{O}^{12}$. Its solution in hydrochloric acid evaporated over sulphuric acid deposits large, pale yellow, tabular crystals of the salt, $2\text{BiBr}^3 \cdot 5\text{NH}^3\text{Cl} + \text{H}^2\text{O}$, analogous to the double chloride, $2\text{BiCl}^3 \cdot 5\text{NH}^3\text{Cl}$, described by Déhérain (*1st Suppl.* 347). This bromochloride is immediately decomposed by water, yielding a milky liquid, probably containing both oxychloride and oxybromide of bismuth.

Oxybromides.—The compound, $\text{Bi}^2\text{Br}^3\text{O}^{12} = 3\text{Bi}^2\text{O}^4 \cdot 2\text{BiBr}^3$, is formed: (1.) As a secondary product in the preparation of the tribromide by heating bismuth with bromine in contact with air, and remains after the volatilisation of the tribromide in the form of a greyish-yellow non-volatile powder. (2.) By the action of gaseous nitrogen trioxide (obtained by heating starch with nitric acid) on fused bismuth tribromide. It is insoluble in water, but dissolves easily in strong nitric and hydrochloric acid, less easily in dilute nitric acid. It is not altered by contact with the air. When heated with charcoal, it is reduced, with formation of tribromide. Heated to low redness in a stream of hydrogen, it becomes reddish-brown, and finally black, a bismuth compound being at the same time mechanically carried forward by the stream of gas:

the final product of the action is metallic bismuth (Muir, *Chem. Soc. J.* 1876, ii. 12; 1877, ii. 137).

Another oxybromide, $\text{Bi}^{11}\text{Br}^7\text{O}^{18} = 7\text{BiOBr} \cdot 2\text{Bi}^2\text{O}^3$, perhaps *bismuthyl oxybromide*, $(\text{BiO})^{11}\text{Br}^7\text{O}^{18}$, is formed by gently heating dry bismuth trioxide for several hours with excess of bromine. It is a cream-coloured, amorphous, non-deliquescent powder, not altered by exposure to the air. When heated it becomes slightly darker, but does not decompose, and the original colour is restored on cooling. The compound is insoluble in water, whether hot or cold; it dissolves easily in hydrochloric and nitric acids, the latter if concentrated giving rise to disengagement of bromine (Muir, *ibid.* 1877, i. 26).

3. *Bismuthyl bromide*, BiOBr , appears to be formed by heating the trioxide with the tribromide (Muir).

Chlorides. The trichloride, BiCl_3 , is easily prepared by passing dry chlorine into a retort containing powdered bismuth; the retort is tilted upwards, and the tube which conducts the chlorine is connected with the beak of the retort. In order to avoid the introduction of moisture from the air, a tube passes through a tightly fitting cork in the tubulus of the retort into a drying cylinder containing strong sulphuric acid, from whence the excess of chlorine is conducted to the draught-chamber. The chlorine and bismuth unite readily, forming in the first instance a black fusible substance, consisting of the dichloride, Bi^2Cl^4 ; but this, after awhile, gives place to a clear, light amber-yellow liquid which, on long-continued but gentle heating, is resolved into metallic bismuth and the trichloride, the latter subliming in crystals which melt at $225^\circ\text{--}230^\circ$. The trichloride, gently heated in a stream of hydrogen, is reduced to the black dichloride, which however at a higher temperature, is decomposed as above into Bi and BiCl_3 . It does not appear possible to obtain a chloride of bismuth higher than the trichloride (Muir, *Chem. Soc. J.* 1876, i. 144).

Oxychlorides.—The only oxychloride of bismuth hitherto known is bismuthyl chloride, BiOCl , formed by the action of water on the trichloride, or by pouring bismuth nitrate into a solution of common salt (i. 591). Muir (*Chem. Soc. Jour.* 1877, ii. 134) has obtained another: (1). On gently heating the trichloride between two watch-glasses, one portion of that compound sublimes in crystals, while the remainder is converted by oxidation into a reddish-yellow, highly crystalline, heavy powder, which may be freed from undecomposed trichloride by washing with water, the light bismuthyl chloride thereby produced being easily separated by levigation. (2.) By the action of nitrogen trioxide on fused bismuth trichloride. The oxychloride prepared by either of these processes gives, as a mean result of analysis, 81.86 per cent. bismuth, 13.63 chlorine, and (by difference) 4.61 oxygen, a result which agrees equally well with either of the formulæ $\text{Bi}^2\text{Cl}^3\text{O}^2 = \text{Bi}(\text{BiO})^2\text{Cl}^3$, or, $\text{Bi}^2\text{Cl}^3\text{O}^2 = \text{Bi}^2\text{O}^3 \cdot \text{Bi}^2\text{Cl}^3$.

This oxychloride of bismuth is permanent in the air, insoluble in water, and not decomposed thereby. It dissolves in hot hydrochloric or nitric acid, less readily in hot sulphuric acid. When boiled with caustic soda, it slowly gives up its chlorine, and is converted into trioxide. It is not changed by heating over a Bunsen lamp, but at an incipient white heat it gives off white fumes, and melts to a yellowish pasty mass containing a considerable quantity of chlorine, and apparently consisting of undecomposed oxychloride. By gentle heating in dry hydrogen it is gradually reduced to metallic bismuth.

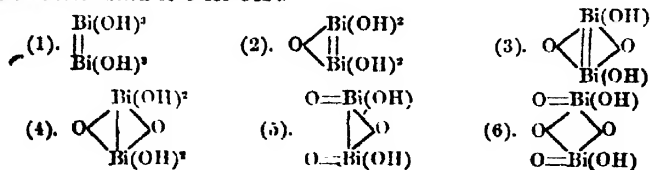
The action of chlorine on hot bismuth trioxide produces nothing but the trichloride.

On *Ferricyanides of Bismuth*, see **CYANIDES**.

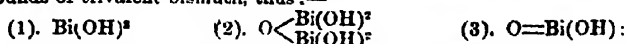
Oxides and Hydrates (Muir, *Chem. Soc. Jour.* 1876, i. 149; 1877, i. 29, 647; ii. 128). The following hydrates of bismuth are known:—

- | | | |
|---|--|--|
| (1). $\text{Bi}^2\text{O}^3 \cdot 3\text{H}^2\text{O}$
Bismuthous Trihydrate. | (2). $\text{Bi}^2\text{O}^3 \cdot 2\text{H}^2\text{O}$
Bismuthous Dihydrate. | (3). $\text{Bi}^2\text{O}^3 \cdot \text{H}^2\text{O}$
Bismuthous Monohydrate. |
| (4). $\text{Bi}^2\text{O}^4 \cdot 2\text{H}^2\text{O}$
Hypobismuthic
Dihydrate. | (5). $\text{Bi}^2\text{O}^4 \cdot \text{H}^2\text{O}$
Hypobismuthic
Monohydrate. | (6). $\text{Bi}^2\text{O}^4 \cdot \text{H}^2\text{O}$
Bismuthic
Hydrate. |

Regarding bismuth as quivalent, these six hydrates may be represented by the following constitutional formulæ, which exhibit their formation one from the other by successive substitution of O for OH:—



The hydrates 4 and 5 are obtained from 1, 2, or 3 by the action of oxidising agents; 6 is produced from the others by the action of very energetic oxidisers, and is easily reconverted into 1, 2, or 3. The three bismuthous hydrates may also be represented as compounds of trivalent bismuth, thus:—



and bismuthic hydrate may be represented by the simpler formula, $\text{BiHO}^3 = \text{BiO}^2(\text{OH})$, analogous to that of nitric acid.

Bismuthic hydrate is prepared by the action of chlorine on the trioxide suspended in a solution of caustic potash (i. 594). It is, however, very apt to retain potash; and to obtain a pure product it is necessary to use very strong potash, continue the passage of the chlorine till the whole of the trioxide is converted into a dense chocolate-red powder, subject this powder to prolonged washing with boiling water, then warm it gently with strong nitric acid for a few seconds only, and finally wash away the acid with water.

Bismuthic hydrate, heated to 120° , gives off water and leaves the pentoxide, Bi_2O_5 . This oxide begins to give off oxygen at 150° , is reduced to tetroxide, Bi_2O_4 , at 225° , and to trioxide, Bi_2O_3 , at a somewhat higher temperature.

Bismuthic hydrate dissolves easily in strong hydrochloric acid, with evolution of chlorine; in strong sulphuric acid only after prolonged digestion. Each of these solutions gives with caustic potash a pale yellowish-white flocculent precipitate, that from the hydrochloric acid solution consisting of $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and that from the sulphuric acid solution of $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

The hydrogen in bismuthic hydrate is not replaceable by metals; in other words, there are no salts of bismuth analogous to the nitrates or metaphosphates. Arppe, indeed, described an acid bismuthate of potassium, Bi^3KHO^3 , said to be obtained by boiling bismuthic hydrate with potash (i. 595). Muir, however, finds that not a trace of bismuth is taken up in this process, the solution containing nothing but potassium hydrate mixed with carbonate. Neither can an ammonium bismuthate be obtained by similar treatment, nor a potassium bismuthate by fusing either of the oxides or the metal itself with potash.

Hypobismuthic Hydrates.—The monohydrate, $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{O} \begin{array}{c} \text{BiO(OH)} \\ \text{BiO(OH)} \end{array}$, is

obtained by the action of chlorine on bismuthous oxide suspended in a solution of caustic potash somewhat weaker than that required for the preparation of bismuthic hydrate, the passage of the gas being stopped as soon as the oxide is transformed into a chocolate-brown powder. On washing this powder till it is free from alkali, and boiling it for a few minutes with a little strong nitric acid, a reddish-yellow substance is obtained, which, when washed free from acid and dried over sulphuric acid, presents the appearance of a brownish-yellow amorphous powder.

This substance is hypobismuthic hydrate. It remains unaltered at 100° , gives off 3.73 per cent. water at 130° ; 4.26 per cent. (in all) at 160° ; becomes dark brown without further loss of water at 190° ; begins to decompose at about 250° ; and when heated over a lamp, quickly becomes light yellow, indicating the conversion of the bismuthous-bismuthic oxide into bismuthous oxide.

Hypobismuthic hydrate is insoluble in water, whether hot or cold; dissolves readily in hydrochloric acid with evolution of chlorine; very slowly in strong nitric acid. It does not form a potassium salt when boiled with potash (Muir).

Hypobismuthic Dihydrate, $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, is formed, according to Schrader (*Liebig's Annalen*, cxxi. 204), by passing chlorine into caustic potash-solution of sp. gr. 1.385, in which bismuthous oxide is suspended, and boiling the red or brown substance thereby obtained with strong nitric acid. It gives off its water at 150° , and becomes light-brown, but is reconverted into the original hydrate by boiling in the dry state with nitric acid.

Hypobismuthous Oxide, or Bismuth Dioxide, $\text{Bi}_2\text{O}_2 = \begin{array}{c} \text{Bi}=\text{O} \\ | \\ \text{Bi}=\text{O} \end{array}$.—This oxide

is formed by the action of the air on metallic bismuth, heated a few degrees above its melting point, and by the action of various reducing agents on bismuthous salts. Schneider prepared it by dissolving Bi_2O_3 and SnCl_2 in equivalent proportions in hydrochloric acid, pouring the solution into rather strong aqueous potash, and washing the resulting black-brown precipitate of SnO_2 and Bi_2O_3 with strong potash, which removes the stannic oxide (1st Suppl. 348). Muir recommends that the washing with potash be conducted in a stoppered flask nearly filled with the liquid, and the resulting oxide dried in a vacuum over sulphuric acid. As thus prepared, it is a black, non-metallic, finely crystalline powder. Schneider states that it is very easily

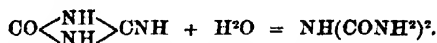
oxidisable, burning in the air like tinder. Muir, on the other hand finds that it oxidises slowly in the air when moist, passing into bismuthous dihydrate, $\text{Bi}^2\text{O}^3 \cdot 2\text{H}^2\text{O}$, but that when dried it remains perfectly unaltered in the air for a considerable time. Heated in the air to 180° it changes colour very slowly, but when heated over a Bunsen flame it is at once converted into the yellow trioxide. It is easily reduced to metal by heating on charcoal in the inner blow-pipe flame, or in hydrogen or carbon monoxide; heated in carbon dioxide, on the other hand, it undergoes slow oxidation. A boiling concentrated solution of potash decomposes hypobismuthous oxide, separating metallic bismuth. Hot dilute hydrochloric acid dissolves it partially, also leaving metallic bismuth. Dilute sulphuric acid acts similarly, but dissolves a much smaller quantity of the oxide. Dilute nitric acid dissolves it readily.

On **OXY-SALTS OF BISMUTH** (Chromates, Stannates, Thiosulphates), see the several ACRES.

BISMUTHINITE. Native bismuth trisulphide (p. 327).

BISMUTITE. Native bismuth carbonate (p. 326).

BIURET, $\text{C}^2\text{H}^4\text{N}^4\text{O}^2 = \text{NH} \begin{smallmatrix} \text{CONH}^2 \\ \text{CONH}^2 \end{smallmatrix}$. This compound is formed by heating amidodicyanic acid with a mixture of 1 pt. strong sulphuric acid and 2 pts. water for some hours to 60° – 70° :—



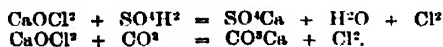
A mixture of equal parts of water and strong nitric acid produces the same effect; strong hydrochloric acid acts but slowly (E. Baumann, *Deut. Chem. Ges. Ber.* viii. 708).

Silver-compounds.—When 2 mols. of silver nitrate are added to a saturated aqueous solution of 1 mol. of biuret, and then gradually ammonia or dilute soda, a white precipitate is formed, which soon blackens on exposure to light, and has the composition $\text{C}^2\text{H}^4\text{Ag}^2\text{N}^4\text{O}^2$. It is readily soluble in nitric acid and ammonia, and sparingly in soda. By decomposing it with hydrogen sulphide in presence of water, biuret is re-produced, and on heating the dry compound in the absence of air to 270° – 280° , water and a little carbon dioxide and ammonia are given off, and a mixture of silver cyanide and paracyanide is left behind. These results are in contradiction to Finckh's statement (1st Suppl. 350), according to which the above reaction gives rise to a precipitate having the composition of silver cyanurate, while the solution contains urea. Finckh probably used an impure biuret containing urea (Bonné a. Goldenberg, *Deut. Chem. Ges. Ber.* vii. 287).

Tripropyl-biuret, $\text{C}^6\text{H}^{12}(\text{C}^2\text{H}^4)^3\text{N}^4\text{O}^2$, is formed, together with propylene, on distilling a mixture of propylsulphate and cyanate of potassium. The propylene goes off as gas, and a yellowish solid distillate is obtained, which, after crystallisation from alcohol, has the composition of tripropyl-biuret (Römer, *Deut. Chem. Ges. Ber.* vi. 784).

BIXIN. When an alcoholic extract of annatto is treated with sodium carbonate, a sodium-compound of bixin is formed, crystallising in leaflets having a coppery lustre; and from this salt, the colouring-matter may be obtained in the crystalline form (C. Etti, *Deut. Chem. Ges. Ber.* vii. 446).

BLEACHING POWDER. The constitution of this substance has lately been made the subject of numerous investigations. Göpner (*J. pr. Chem.* [2], vii. 441) has endeavoured to revive the old view that bleaching powder is a direct compound of chlorine with lime, $\text{CaO} \cdot \text{Cl}^2$, on the ground that when distilled with aqueous acids, or exposed to the action of carbon dioxide, it gives off only chlorine unmixed with chlorine monoxide :—



The constant presence of calcium chloride in bleaching powder is attributed by Göpner to the action of hydrochloric acid and carbon dioxide mixed with the chlorine gas, the carbon dioxide first producing calcium carbonate, which is then decomposed by the chlorine according to the equation :—

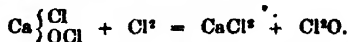


The same view of the constitution of bleaching powder is advocated by Richter a. Juncker (*Dingl. pol. J.* cxx. 21; cxxii. 339).

Schorlemmer, on the other hand, remarks (*Deut. Chem. Ges. Ber.* vi. 1509; *Chem. Soc. Jour.* [2], xii. 335) that hypochlorous acid is very easily obtained by distilling

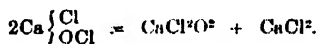
bleaching powder with the requisite quantity of nitric acid, a colourless distillate being thereby produced, which bleaches much more strongly than recently prepared chlorine-water, and when shaken up with mercury yields a considerable quantity of brown mercuric oxychloride (*Gmelin's Handbook*, vi. 60). The fact that when bleaching powder is exhausted with successive small quantities of water, the last extracts still contain calcium and chlorine in the proportions required by the formula, CaOCl_2 , merely shows that the product of the action of chlorine on lime is not a mixture of calcium chloride and hypochlorite, ($\text{CaCl}_2 + \text{CaCl}^2\text{O}^2$), but a compound constituted according to the formula, $\text{Ca} \begin{Bmatrix} \text{Cl} \\ \text{OCl} \end{Bmatrix}$, as first suggested by Odling.

In the preparation of aqueous hypochlorous acid by the action of chlorine on water containing calcium carbonate in suspension, the compound just mentioned is first formed and then decomposed according to the equation:—



See further Göpner (*Deut. Chem. Ges. Ber.* vii. 270; Schorlemmer, *ibid.* 682).

This view of the constitution of bleaching powder is corroborated by the recent experiments of Kingzett and of Kopfer. Kingzett (*Chem. Soc. Jour.* [2], xiii. 404) finds that bleaching powder when treated with water is gradually resolved into chloride and hypochlorite of calcium, the latter of which may be separated in the crystalline form by exposing the filtered solution to a freezing mixture, or by evaporating it in a vacuum over oil of vitriol. A dense frozen crystalline mass is then obtained, and on leaving this mass to thaw upon a filter, a solution of calcium chloride mixed with hypochlorite passes through, and feathery crystals remain on the filter, very unstable but consisting, when recently prepared, of hydrated calcium hypochlorite, $\text{CaCl}^2\text{O}^2 + 4\text{H}^2\text{O}$. These crystals smell of hypochlorous acid, and are decomposed by acids, with evolution of chlorine. These results show that the bleaching powder contains either ready-formed calcium hypochlorite mixed with chloride, or a compound, $\text{CaCl}(\text{OCl})$, from which the hypochlorite may be formed by the action of water—



If, however, it consisted of a mixture of the two salts in the proportion indicated by this formula, it ought to yield to alcohol a quantity of calcium chloride equivalent to half the total quantity of calcium or of chlorine contained in it, which is not the case: hence it must be supposed to have the constitution represented by Odling's formula.

Kopfer (*Chem. Soc. Jour.* [2], xiii. 713) has studied the decomposition of bleaching powder by the action of dilute acids. The bleaching powder was prepared by the action of chlorine on slaked lime obtained by calcination of pure carbonate or nitrate of calcium, and was found to have the following composition:—

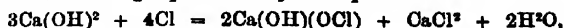
Calcium hypochlorite . . .	21.46	, or	$\text{Ca} \begin{Bmatrix} \text{Cl} \\ \text{OCl} \end{Bmatrix}$	38.12
Calcium chloride . . .	17.89		CaCl_2	1.06
Calcium hydrate . . .	47.52		$\text{Ca}(\text{OH})^2$	47.52
Calcium oxide . . .	13.33		CaO	13.33
	100.00			100.00

Now, on treating this powder, either in the dry state or in solution, with a dilute mineral acid, as nitric, hydrochloric, or sulphuric acid, in quantity such as to saturate the caustic lime, and decompose the hypochlorite which may be supposed to be present, an aqueous solution of chlorine monoxide is obtained, almost pure and quite free from the smell of chlorine, the quantity of Cl^2O thus formed, amounting, in the most favourable case, to about 92 per cent. of that which corresponds with the hypothetical hypochlorite. That the solution thus obtained really contains chlorine monoxide is further shown by shaking it up in the cold with a large excess of mercury, whereby the brown oxychloride of mercury is abundantly produced.

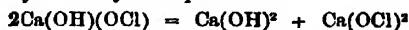
These results therefore agree with those of Kingzett in showing that bleaching powder contains either a mixture of calcium chloride and hypochlorite, or the compound $\text{CaCl}(\text{OCl})$. Both views explain equally well the production of hypochlorous acid, and both account in a satisfactory manner for the formation of bleaching powder by the action of chlorine upon calcium hydroxide. One atom of chlorine first replaces the group OH, which combines in the nascent state with the hydrogen atom of another hydroxyl to form water, whilst the second atom of chlorine goes into the place of the hydrogen atom thus removed.

Further, both views account for the non-production of bleaching powder from anhydrous lime, whilst it is difficult to explain this fact if bleaching powder is supposed to contain a compound of chlorine and calcium oxide. See also Wolters (*J. pr. Chem.* [2], x. 128; *Dingl. pol. J.* cxxiv. 140; *Chem. Soc. Jour.* 1875, 236, 433).

According to Stahl Schmidt, bleaching powder consists of calcium hydroxychloride, $\text{Ca} \begin{Bmatrix} \text{OH} \\ \text{OCl} \end{Bmatrix}$, i.e. calcium hydroxide, $\text{Ca}(\text{OH})^2$, in which 1 at. hydrogen is replaced by chlorine, its formation being represented by the equation:—



and its decomposition by water by the equation:—



(*Deut. Chem. Ges. Ber.* 1875, 869; *Dingl. pol. J.* cxxi. 243, 335; *Chem. Soc. Jour.* 1876, ii. 604; 1877, i. 279).

Manufacture.—From numerous and careful experiments by C. Opl (*Dingl. pol. J.* ccxv. 232, 325), the following conditions appear to be essential to the preparation of good bleaching powder. The chlorine must be free from hydrochloric acid and carbonic acid, and must be passed into the chambers at the lowest possible temperature. The calcium hydrate must be pure, not containing carbonate, and should be used with as much free water as can be added without interfering with the subsequent operation of sifting. The chambers must be kept as cool as possible during the absorption, the temperature not being allowed to rise above 25°C .; they should be so arranged as to admit of easy cleansing. The powder when taken out of the chambers should be well mixed in shallow wooden boxes with lids, and should not be packed for transport till it has cooled down to the temperature of the air, or at least to 21° . If bleaching powder is immediately packed in casks on hot summer days, it invariably decomposes, and sometimes so rapidly as to become worthless in a few hours.

Alteration by Keeping.—J. Pattinson (*Chem. News*, xxix. 143; *Jahresb.* 1873, 243) has made a series of observations on the proportion in which weak and strong bleaching powder give off their active chlorine (that which may be supposed to exist as hypochlorite). Equal weights of different samples of bleaching powder were kept in loosely corked bottles protected from direct sunshine, and the quantities of active chlorine in them were determined from time to time by means of arsenious acid (i. 904). The results showed that the loss of active chlorine is greater in summer than in winter, and that strong bleaching powder does not give off relatively more chlorine than the weaker varieties.

BLOOD. Constituents.—According to C. Bernard (*Arch. Pharm.* [3], iii. 578), blood contains sugar as a normal constituent, independent of the kind of food taken; in the blood of diseased animals, on the other hand, sugar is absent. The formation of the sugar takes place in the liver.

Ash.—The following analyses of the ash of blood have been made by A. Jarisch (*Chem. Centr.* 1877, 7).

	Man		Horse	Ox	Dog	
	Normal	In Pneumonia			Normal	In Fever
P_2O_5	8.61	8.82	8.38	4.98	12.74	12.73
SO_3	11.44	7.11	6.31	6.17	4.13	3.76
Cl	28.63	30.74	28.63	35.12	32.47	33.32
K_2O	22.92	26.55	29.48	10.74	3.96	3.11
Na_2O	26.06	24.11	21.15	37.44	43.40	44.69
CaO	1.24	0.90	1.08	1.15	1.29	1.14
MgO	0.52	0.53	0.60	0.18	0.68	0.40
Fe_2O_3	7.03	8.16	9.52	9.24	8.64	8.36
			CO_2 1.30	2.97		

Iron.—The quantities of iron in the fibrin, blood-corpuscles, and albumin from the blood of a half-fat cow have been determined by Boussingault (*Arch. Pharm.* [3], iii. 526). 100 parts of the dried substances contained:—

	Ash.	Metallic Iron.
Fibrin	2.151	0.0466
Corpuscles	1.325	0.3500
Albumin	8.716	0.0863

100 parts of blood-pigment were found to contain :—

Organic matter	Fe ² O ³	P ² O ⁵	CaO
89.25	0.04	1.45	0.32 = 100.06

In dogs, according to Picard (*Compt. rend.* lxxix. 1266), the amount of iron in the blood is somewhat variable, and proportional to the quantity of oxygen which the blood is capable of absorbing.

According to Paquelin a. Jolly (*Compt. rend.* lxxviii. 1579), the iron in blood is in the form of ferrous, not of ferric phosphate as commonly supposed.

Blood-pigment may be prepared in the pure state as follows :—Defibrinated blood is diluted with water till the corpuscles are disintegrated ; the liquid is then precipitated with basic lead acetate and filtered ; the filtrate is precipitated with basic lead acetate and ammonia ; and from the liquid filtered from this second precipitate the pigment is thrown down by basic lead acetate and alcohol. The lead compound, washed with alcohol, suspended in water, and decomposed by carbonic acid, yields a solution of pure blood-pigment which coagulates at 61°, and when evaporated at 35°-40° leaves the pigment in red lamellæ (Béchamp, *Ann. Chim. Phys.* [5], iii. 340). According to Paquelin a. Jolly, blood-pigment does not contain iron.

Reaction of Blood with Zinc.—According to H. Struve (*J. pr. Chem.* [2], vii. 346 ; *Chem. Centr.* 1874, 475), defibrinated blood, diluted with water, becomes turbid when shaken with zinc or zinc oxide, and deposits a red precipitate. The filtrate contains gelatin, salts, and traces of hydrogen dioxide, but no hæmatin or blood-albumin. Since the oxide of zinc acts in the same manner as the metal itself, Struve concludes that the precipitation of the blood-pigment and the albumin is due to the formation of zinc carbonate, the metal abstracting oxygen and carbonic acid from the blood. If, after the precipitation of the blood-pigment and the albumin by zinc, a stream of carbon dioxide be passed through the liquid, the precipitate redissolves, and the filtered solution gives neither the spectrum of oxyhæmoglobin nor that of meta-hæmoglobin. If a continued stream of air be passed through the liquid thus treated with carbon dioxide, the precipitate formed by the zinc reappears, but is redissolved by the carbonic acid.

When fresh blood, still containing corpuscles, is treated with zinc, the resulting precipitate exhibits the form of these corpuscles, even if it has remained under the liquid for months, provided the zinc has been left in contact with the liquid. If the zinc is left in contact with the precipitate, an evolution of gas gradually sets in and lasts for a long time, the blood-pigment at the same time undergoing a radical alteration.

Action of Ozone.—This action is exerted chiefly on the blood-corpuscles, their colouring matter being separated and the blood becoming darker after a quarter of an hour. Defibrinated blood, exposed in thin layers to the prolonged action of ozone, becomes brownish-yellow, and does not yield any crystals of hæmoglobin on addition of alcohol, ether, or chloroform. On passing ozone for a long time through defibrinated blood, flocks are deposited, which, after washing with water, are undistinguishable from fibrin. The formation of this fibrin-like body is probably determined by an alteration of the hæmoglobin. Hæmatin is likewise decolorised by ozone. When blood poisoned by carbonic oxide is subjected to the action of ozone, it quickly recovers the properties of normal blood, and gives off carbonic acid. Blood containing carbonic oxide is less quickly decolorised by ozone than normal blood, and does not so quickly lose the property of depositing crystals of hæmatin. This alteration of the blood-corpuscles by ozone must not be confounded with that which results from the action of carbonic acid (*J. Doziel, N. Rép. Pharm.* xxiv. 231).

Coagulation.—According to Matthieu a. Urbain (*Compt. rend.* lxxix. 666), the coagulation of the blood is determined by carbonic acid, which, when the blood is exposed to the air, is expelled by the oxygen from the corpuscles in which it is held fast during life. On this view it is apparent why alkalis and ammonia, as well as concentrated solutions of many salts, which absorb carbonic acid, prevent the coagulation of blood.

Gautier (*ibid.* lxxxi. 528) finds that the coagulation of blood may be prevented by receiving it in a vessel filled with solution of sodium chloride and then dissolving 4 per cent. of the solid salt in the liquid at 8° ; the blood-corpuscles may then be separated by filtration through paper wetted with salt water, and the plasma thus obtained is a nearly colourless filtrate, which is coagulated by addition of water, but not by the passage of a stream of carbon dioxide. The plasma may be dried up in a vacuum, and heated in the dry state even to 110° without losing the property of coagulating. Gautier infers from these results that the coagulation of the blood is not an act of life or death, and that it is not determined by carbonic acid or by any other of the gaseous constituents of blood. *

Matthieu a. Urbain observe, on the other hand, that the prevention of coagulation of blood at or below 8° by addition of common salt, may be explained by the fact that solutions of common salt take up but a small quantity of carbon dioxide, and that this gas has but little affinity for fibrin at low temperatures. They therefore maintain their opinion that carbon dioxide is the agent which brings about the spontaneous coagulation of blood, and that the fibrin remains dissolved in the plasma during life, because the carbon dioxide is chemically combined with the red blood-corpuscles (*Compt. rend.* lxxxi. 372).

To this Gautier replies (*ibid.* 899) that carbon dioxide cannot be the cause of the coagulation:—1. Because the plasma is still coagulable after it has been dried in a vacuum and heated to 110° , and thereby completely deprived of carbon dioxide. 2. Because no coagulation takes place when carbon dioxide is passed into plasma containing 4 per cent. of common salt, although the quantity of that gas absorbed by the solution is sufficient to produce a considerable separation of fibrin. 3. Because the defibrinated blood contains as much CO_2 as blood still containing fibrin, the coagulation of which has been prevented by common salt.

Matthieu a. Urbain (*Compt. rend.* lxxxii. 422) reply to these remarks that when undiluted blood-plasma is evaporated in a vacuum, the carbon dioxide remains combined with the alkali-salts, and that when this combination is broken up by a sufficient addition of water to the dry blood-plasma, the carbon dioxide thereby set free determines the separation of the fibrin. The non-coagulation at 8° of blood-plasma mixed with 5 per cent. of common salt, may be due to the low temperature and the anti-coagulating action of the salt. Gautier, on the other hand, remarks that sodium bicarbonate is quickly decomposed when its aqueous solution is evaporated under reduced pressure at 26° , whence it follows that the evaporation of blood-plasma in a vacuum is sufficient to determine the decomposition of the bicarbonates contained in it (*ibid.* lxxxiii. 277). To this Urbain replies (*ibid.* 543) that the decomposition of bicarbonates may be regarded as a process of dissociation, at all events that complete decomposition takes place when the carbon dioxide is continually driven away by air or aqueous vapour, but that when the bicarbonate is enveloped in albumin, gum, sugar, or similar substances, as is the case in blood-plasma, it may be heated to 100° without decomposition.

Gases of Blood.—The influence of various circumstances on the quantity of gas in arterial blood has been examined by Matthieu a. Urbain (*Compt. rend.* lxxxiii. 216: *Ann. Ch. Phys.* [5], i. 482). Blood-letting is followed by a diminution of the amount of oxygen, due partly to a loss of blood-corpuscles, but especially to the diminution of the blood-pressure, in consequence of which the velocity of the blood is accelerated and the respiration retarded. The effect of the blood-letting disappears after fifteen to twenty days.

Arteries of equal size contain blood of the same composition, but on comparing the blood in arteries of different diameters it is found that the larger vessels contain blood comparatively rich in oxygen and carbonic acid. The density of the blood is also less in the smaller arteries, inasmuch as the suspended corpuscles, which act as carriers of oxygen, are less able than the surrounding liquid to change the direction of their motion, and consequently flow with less rapidity into the smaller arteries which branch off from the principal vessels. Arterial blood contains more oxygen in winter than in summer. This induces a more active organic combustion, and therefore a quicker renewal of the heat abstracted from the body by the surrounding medium.

Observations on the changes which blood undergoes in the spleen, with regard to the number of its corpuscles, and its power of absorbing oxygen, have been made by Malassez a. Picard (*Compt. rend.* lxxix. 1511).

Blood of the Sea-spider and of Crabs.—The blood of these animals exhibits no absorption-bands: it turns blue when exposed to the air, but loses this blue colour in carbon dioxide. The blood of the crab and of the ray contains considerable quantities of urea (Rabuteau a. Papillon, *Compt. rend.* lxxvii. 133).

Detection of Blood.—Sonnenschein (*Chem. Centralblatt*, 1873, 423) uses for this purpose a solution of sodium tungstate or molybdate strongly acidulated with acetic or tribasic phosphoric acid. Such a solution gives, with solutions of proteids, precipitates which shrink up to a small bulk when heated under the liquid, and solidify on cooling to friable substances. These precipitates, if not too strongly dried, dissolve with aid of heat in alkaline liquids, especially in ammonia. The precipitate thus obtained from blood gives, when dissolved in ammonia, a characteristic green-red dichroic liquid. For the detection of blood-stains, the stained surface must be washed out with water, and the filtered solution treated with the reagent above mentioned. The ammoniacal solution of the precipitate exhibits a distinct coloration

even when the watery extract of the blood-spot appears scarcely coloured. From the ammoniacal solution the precipitate may be thrown down again by acids, and used for the detection of nitrogen (formation of cyanogen by fusion with sodium) or, after incineration, for the detection of the iron in the blood.

For the detection of blood in urine, Almén (*Zeitschr. anal. Chem.* 1874, 104) recommends that a few cubic centimeters of guaiacum tincture be put into a test tube, together with an equal volume of turpentine, and the tube shaken till an emulsion is formed. The urine to be tested is then poured into the tube, and falls to the bottom. If it contains blood, the guaiacum solution becomes more or less blue, whereas with normal urine this coloration is not produced.

According to E. Reichardt (*Arch. Pharm.* [3], vii. 537), the only test for blood that can be safely relied on in judicial inquiries is the formation of blood-crystals on addition of acetic acid. Purpurin-sulphuric acid, obtained by boiling sulphindigotic acid, exhibits, when examined by the spectroscopé, exactly the same appearances as alkaline blood.

On the estimation of Oxygen in Blood by means of Hyposulphurous Acid, see Schützenberger a. Rissler (*2nd Suppl.* p. 200).

BOLEDO. The boldo is a tree indigenous in Chili, and belonging to the order *Monimiaceae*. It is the *Boldoa fragrans* of Jussieu, the *Ruizia fragrans* of Ruiz and Pavon, and the *Pennus fragrans* of Porsoz. Baillon has recently described it under the name of *Pennus boldus*. The leaves contain an essential oil and an alkaloid.

The latter, which does not appear to be crystallisable, is very slightly soluble in water, to which, however, it communicates an alkaline reaction and bitter taste. It is soluble in alcohol, ether, chloroform, caustic alkalis, and benzene. From solution in acids it is precipitated by ammonia and by the double iodide of mercury and potassium; with solution of iodine it gives a chestnut-brown precipitate. Strong nitric acid immediately colours it red, and it assumes the same coloration in the cold with sulphuric acid (Bourgoin a. Verne, *Bull. Soc. Chim.* [2], xviii. 481; *Pharm. J. Trans.* [3], iii. 323).

BOLE. This mineral is generally regarded as a hydrated silicate of aluminium having the alumina partly replaced by ferric oxide, or containing ferric hydrate as an admixture. The small quantities of other bodies present have also been looked upon as admixtures. Kenngott, however, from the examination of numerous specimens, finds that the mineral fuses easily to a yellowish- to brownish-green glassy mass, showing that it cannot consist essentially of aluminium and iron silicate, but must also contain some other constituent, to which the fusibility is due; and this conclusion agrees with the results of experiments made by Rammelsberg on boles from numerous localities, from all of which, by digesting small fragments for some time in hydrochloric acid, and then adding to the liquid a small quantity of sulphuric acid, he obtained slender needles of gypsum, showing that these boles contained lime (*Jahrbuch f. Mineralogie*, 1874, 171).

BONE. F. Wibel (*J. pr. Chem.* [2], ix. 113) objects to Aëby's view of the composition of bone phosphate (*2nd Suppl.* 974), according to which this phosphate is a compound of calcic orthophosphate, water of crystallisation, calcic hydrate, and carbon dioxide, and gives the preference to the older view that fresh bone-substance is a mixture of calcic orthophosphate, $(\text{PO}_4)_2\text{Ca}^2$, calcic carbonate, and ossein. He points out that the composition of fresh bone-substance cannot be correctly inferred from that of fossil ivory, since bone phosphate is known to be altered in composition by the action of water and carbonic acid. Aëby found that the carbon dioxide expelled from bone-substance by ignition is only partly restored by treating the ignited mass with ammonium carbonate, and thence inferred that carbon dioxide exists in bone in two different states. Wibel, however, finds that the result just mentioned is not peculiar to bone, but that artificial mixtures of calcium phosphate and carbonate act on one another, when ignited, in such a manner that only a part of the carbon dioxide present in the unignited mass can be restored by the action of ammonium carbonate. Hence it follows that in the analysis of bone-substance, guano, and certain phosphates, the determination of carbonic acid, to be correct, must be performed upon the unignited substance.

Aëby, on the other hand (*J. pr. Chem.* [2], ix. 469), adduces, in support of his views, the transformations exhibited by the bones found in pile-dwellings. In these bones calcium fluoride is present to the amount of 4 per cent., and the difference in the amount of carbon dioxide before and after ignition is much less than in recent bones, while the basic calcium phosphate has remained unaltered. These changes are due, according to Aëby, to the action of alkaline fluorides on a mixture of salts containing phosphoric and carbonic acids. He supposes that both ivory and bone

BONES

contain as an essential constituent a polybasic phosphate, the former containing the elements of orthophosphate together with hydrate and carbonate, the latter the elements of orthophosphate and carbonate. The carbonic acid appears to be but loosely combined.

From experiments by Schrodtt, however (*Landw. Versuchs. Stationen*. xix. 349), it appears that the quantity of lime in bones is not sufficient even to justify the conclusion that the earthy matter of bones is a mixture of tricalcic phosphate and carbonate. The experiments were made on the bones of a dog, the carbonic acid being determined both in the raw bones and in the ash. On deducting from the total amount of lime, that required for the saturation of the carbonic acid, and combining the remainder with the phosphoric acid to form tricalcic phosphate, there remained in every case an excess of phosphoric acid unaccounted for. Hence Schrodtt infers that the phosphate of bones is partly tribasic, partly bibasic.

Effects of various Solvents on Bone-substance.—Maly a. Donath (*J. pr. Chem.* [2], vii. 413) find that water exerts a nearly equal solvent power on calcium phosphate, gelatinous or ignited, and on bone-substance; also that the inorganic matter of bones is dissolved by aqueous carbonic acid and sal-ammoniac more readily than by distilled water, less abundantly by solutions of bile, common salt, gelatin, sugar, sodium bicarbonate, lactate, and phosphate. From the results obtained by the action of bones, freed from their inorganic constituents, on calcium phosphate under various conditions, and from the examination of precipitates of calcium phosphate produced in solutions of gelatin, Maly a. Donath infer that the inorganic and organic constituents of bone are not chemically combined, but merely mechanically mixed. The same view is taken by Aebv (*ibid.* x. 408).

Variations in the Composition of the Bones depending on Diet, &c.—The bones of a young pigeon, fed for seven months on corn which had been rolled in a thin paste made up of strontium phosphate and a solution of $1\frac{1}{2}$ grams potassium chloride, nitrate, sulphate, and carbonate in a litre of water, were found to contain 46.75 per cent. lime, 8.45 strontia, 41.8 phosphoric acid, 1.80 magnesium phosphate, and 1.10 residue. A young white rat was fed with rice and gluten which had been treated with aluminium phosphate and the same solution: it died of enteritis. 100 parts of its calcined bones were found to contain 6.95 pts. alumina and 41.10 lime. Another rat of the same age was fed for a shorter time on similar food containing magnesium phosphate instead of aluminium phosphate. The ash of its bones contained in 100 pts. 3.56 pts. magnesia and 46.15 lime (Papillon, *Compt. rend.* lxxi. 372).

Papillon has also examined the bones of pigeons, fowls, and the so-called 'crab's eyes,' after the animals had been fed on a diet containing magnesium salts to the exclusion of lime salts. The proportion of magnesia in the bones was found to be sensibly in excess of the normal amount, though the quantity taken up was much less than that of the strontia in the experiments above mentioned.

On the other hand, Weiske-Proskau (*Zeitschr. f. Biologie*, viii. 239), from a repetition of Papillon's experiments, infers that the composition of the bones is not altered by the introduction of foreign salts into the diet. In the bones of rabbits fed on a diet containing strontium and magnesium phosphates, he could not detect the slightest trace of strontia or any notable increase in the proportion of magnesia or phosphoric acid. The age of the animal has some influence on the composition of the bones, those of old rabbits containing a larger proportion of mineral salts. The average proportion of phosphoric acid is nearly the same in all bones, viz., 42.17 per cent. A full-grown goat fed on a diet deficient in lime and phosphoric acid, suffered in health and ultimately died, but its bones exhibited no deviation from the normal composition. Similar results were obtained by experiments on lambs (*Chem. Centr.* 1872, 409; 1874, 123).

Results contrary to these have however been obtained by J. Forster (*Zeitschr. f. Biologie*, xii. 464). From experiments on dogs he infers that with a diet containing an insufficient quantity of lime, but sufficing to sustain the albuminous constituents of the organism, all the organs, more especially the muscles, and also the skeleton, become partially impoverished in lime, without any diminution in the organic substances of the body taking place. The quantity of lime contained in a diet consisting exclusively of meat, does not suffice to sustain the amount of lime in the body, although its albuminous constituents may remain unchanged.

Weiske's failure to observe, in animals receiving an insufficient supply of lime, either a partial loss of lime in the skeleton, or the occurrence of disease of the bones, may be explained by the following considerations:—(1.) Conclusions with regard to the composition of the whole skeleton must not be drawn from an analysis of individual bones. (2.) The nourishment of the animals under experiment should be such that,

whilst losing lime, they may not suffer a diminution in combustible substances. For with a generally insufficient supply of nourishment as well as a deficiency of lime, both soft parts and bones diminish, and the ash-components which are thus set free, may, under certain circumstances, be used again without being excreted from the body.

The deficiency of inorganic constituents in the bones observed during certain diseases, as rachitis and osteomalacia, has been attributed by some physiologists to the solvent action of lactic acid generated in the intestines by the fermentation of carbohydrates; and, according to Heismann, rachitis and osteomalacia may be produced in animals by the administration of lactic acid, either in the food or by subcutaneous injection: he did not, however, analyse the bones of the animals thus treated.

Results of opposite character have been obtained by E. Heiss (*Zeitschr. f. Biol.* xii. 151), who fed a small dog, weighing 4·7 kilograms, for 308 days on food containing lactic acid to the amount of 1 to 2 grams at first, afterwards increased to 4 to 6 grams, and finally to 7 to 9 grams. During the whole time the dog continued in good health, and when it was killed, its bones showed no signs of rachitis or osteomalacia; and the different parts of its body were found to contain their normal proportions of mineral constituents, showing no deficiency in the alkaline earths. The total amounts of lime and magnesia in the food were found to be exactly the same as those excreted in the dung and urine, showing that none had been withdrawn by the lactic acid. This acid appeared indeed to have been decomposed in passing through the dog's body, as none was found in the urine.

BONE-BLACK. Processes for the carbonisation of bones, and the preparation of ammonia-salts and bone-oil from the products of the distillation, are given by Sebor (*Dingl. pol. J.* cccviii. 350), and by Dunod & Bougleux (*American Chemist*, iii. 265).

A method for the revivification of bone-charcoal in sugar-works by the use of sal-ammoniac is described by C. Preis (*Dingl. pol. J.* ccc. 396). On boiling the spent charcoal with a dilute solution of sal-ammoniac, the calcium carbonate contained in it is dissolved, and the ammonium carbonate thereby evolved acts upon the organic substances absorbed by the charcoal.

Valuation.—J. B. Schober (*N. Rep. Pharm.* xxii. 267) estimates the value of bone-black by its action on a solution of indigo of known strength. A solution of indigo-carmin (6 grams to a litre) is standardised by a solution of potassium permanganate containing 1 gram of the salt in 1000 c.c. of water; 1 gram of the charcoal is added to 50 c.c. of the indigo-solution in a flask; the whole well shaken, boiled, and left at rest for twenty-four hours; and the proportion of indigo remaining unabsorbed is then determined by the permanganate in an aliquot part of the liquid filtered from the charcoal.

With reference to this process, C. H. Gill observes that, like all other methods of estimation depending on the absorbing or decolorising power of the charcoal, its results are affected by the initial difficulty of reducing the various samples to the same state of division, without which the same specimen will give results differing from one another as much as any two from different sources (*Chem. Soc. J.* 1873, p. 1060).

K. Vierordt (*Pogg. Ann.* cxlix. 565) observes that all the colorimetric methods hitherto adopted for determining the decolorising power of bone-charcoal, are affected by an uncertainty arising from the use of white light in judging of the colour. To avoid this source of error, he proposes to use only that part of the spectrum for which the colour under examination exhibits the maximum degree of absorption. For molasses, this part of the spectrum lies between F and F 10 G; for practical purposes, the portion from F to F 20 G will give sufficiently accurate results. Even if the absolute quantity of colouring matter in a sample of molasses cannot be thus determined, it is easy to estimate the relative amounts in different samples. These amounts are proportional to the coefficients of extinction, i.e. to the negative logarithms of the quantities of light of a particular region of the spectrum, which remain unabsorbed after the light has traversed a layer of the absorbent fluid, 1 c.c. in thickness. The maximum action of the charcoal is exerted only after twenty-four hours' contact with the coloured liquid; nevertheless it is possible to obtain numbers sufficient for the comparison of different charcoals, by continuing the action for shorter, but always equal times.

If the weight in grams of the charcoal (e. g. 2 grams) be denoted by K, the volume of the molasses (e. g. 10 c.c.) by v, the amount of colouring matter in the molasses by c, that of the decolorised solution by C (c and C being determined as above), then, if the light used is that of the spectrum between F and F 10 G, we have

$$C = \frac{v \cdot c^2}{K} \gamma,$$

where γ is a coefficient depending on the decolorising power of the charcoal.

From the preceding equation it follows that

$$\gamma = \frac{C \cdot K}{v \cdot d^2}$$

Taking therefore equal quantities of charcoal, equal volumes of molasses, and a constant amount of colouring matter (*e. g.* a brown syrup diluted to one-fourth) the relative value of any sample of charcoal will be expressed simply by the coefficient of extinction answering to the intensity of the light observed in the region of the spectrum from F to F 10 G. The charcoal examined by Viorordt gave $\gamma = 0.00304$.

Estimation of Organic Matter in Bone-black.—For this purpose, W. Thorn (*Dingl. pol. J.* cccvi. 268) boils the charcoal with dilute soda-ley, and, after acidulating the filtered liquid thereby obtained, titrates it with solution of permanganate, assuming, according to Wood's determination (*Chem. Soc. J.* 1863, p. 62), that 1 pt. of potassium permanganate is capable of oxidising 5 pts. of organic matter.

On the occurrence of Iron Sulphide in Bone-black, see R. F. Smith (*Chem. News*, xxx. 171, 202, 217, 233, 240, 261, 293).

Absorption of Gypsum-solutions by Bone-black.—When a solution of gypsum is filtered through well-washed bone-black, the gypsum is at first decomposed by the ammoniacal salts which are always present in the charcoal, lime being retained and ammonium sulphate passing into the solution. At the same time, however, the gypsum is absorbed as such, but so loosely that it may be extracted by prolonged washing with water. In an experiment in which 500 c.c. of gypsum solution containing 16.3 grams of gypsum were filtered through 36.4 grams of finely powdered bone-black, 7.19 grams of gypsum were absorbed as such, 4.93 grams were decomposed, and 4.18 grams passed through without alteration. The charcoal subsequently yielded to water 0.18 grams of gypsum (*E. Anthon, Dingl. pol. J.* ccciii. 159).

Action of Bone-black on Ammonium Salts. From a dilute aqueous solution of ammonia, bone-black abstracts only a small quantity of ammonia. Ammonium salts also are but slightly absorbed, and generally decomposed to a small extent at the same time. This decomposition is greater in amount with the ammonium salts of polybasic acids than with those of monobasic acids. The acetate, for example, is absorbed almost without decomposition, whereas the neutral sulphate gives up part of its ammonia, and is more or less converted into acid salt. If the resulting acid salts are easily soluble, they are but slightly absorbed by the charcoal; but if they are but slightly soluble (ammonio-potassic tartrate for example), or capable of forming insoluble compounds with any of the constituents of the bone-charcoal, the acids appear to be absorbed in greater proportion than the ammonia. The absorption of ammonium salts by the charcoal appears to be favoured by rise of temperature (Birnbbaum & Bomasch, *Dingl. pol. J.* cccviii. 148).

Reducing Action of Bone-Charcoal at Low Temperatures.—When a solution of platinum chloride is boiled for some time with freshly ignited bone-charcoal, a colourless acid solution results, containing no platinum and leaving scarcely any residue on evaporation (provided the charcoal has been previously freed from all matters soluble in hydrochloric acid). A solution of dehydrotriacetnammonium platinochloride is partially reduced on boiling with animal charcoal, the platinum becoming platinumous chloride, so that the original salt is regenerated on adding chlorine-water.

Ferrous Chloride is easily reduced to ferrous chloride by bone-charcoal, a trace of organic substance passing into solution, but no gaseous oxide of carbon or any other carbonaceous gas being given off: hence it would appear that the reduction is mainly due to the hydrogen which still remains in the charcoal, even after strong ignition (Heintz, *Liebig's Annalen*, clxxxvii. 227).

Artificial Bone-black.—Gawalovski (*Dingl. pol. J.* ccciv. 258) suggests the preparation of a substitute for bone-charcoal by saturating lumps of pumice of the size of a walnut with blood in a vacuum, and then igniting them in a closed vessel. The product is a shining black charcoal, which adheres to the tongue, and is capable of nearly decolorising a reddish-yellow sugar-beet juice after half-an-hour's digestion; the alkalinity of the juice treated with it was not however diminished. Gawalovski is of opinion that the salt in the blood-ash interferes with the action, and considers it essential that the charcoal should be thoroughly washed before being used.

According to Melsens (*Compt. rend.* lxxix. 376) the only way of obtaining an efficient substitute for animal charcoal is to saturate wood with a solution of calcium phosphate, and then to carbonise it. It is difficult, however, to obtain a preparation containing a sufficient quantity of mineral matter. The charcoal must be well washed before use to free it from calcium chloride.

The following forms of this mineral have been described by A. Schrauf (*Jahrb. f. Min.* 1873, 960).

Boracite.—(1). $\infty O \infty O \infty \frac{O}{2} . 202$, from Lüneburg.—(2). $\infty O \infty . \infty O . \frac{O}{2} - \frac{O}{2} . 202$, 50 $\frac{1}{2}$, from Lüneburg.—(3). $\frac{O}{2} . \infty O \infty . \infty O - \frac{O}{2}$, also from Lüneburg, with parallel repetition.—(4). $\infty O \infty$ (very predominant), $\frac{O}{2} . \infty O . \infty O 3$: loose crystals from Stassfurt.—(5). $\infty O \infty$ (predominant) $\frac{O}{2} - \frac{O}{2} . \infty O . \frac{1}{2} O$.—(6). $\infty O \infty . \frac{O}{2}$, twin; for the intersecting twin, the twin-face is a face of the positive tetrahedron.

BORNEOL, $C^{10}H^{16}O$. On the constitutional formula of this body, see CAMPHOR.

Supposed Allotropic modifications.—Wöhler & Deville, in 1857, by heating aluminium with boric oxide or amorphous boron, obtained two classes of crystals, black and yellow, which were regarded by them, and have since been regarded, as varieties of crystallised boron (i. 628). But from recent experiments by W. Hempo (*Liebig's Annalen*, cxxxiii. 76), who has repeatedly prepared and analysed these crystals, it appears that they are not really pure boron, but compounds of that element with aluminium or with aluminium and carbon.

The black crystals (Wöhler and Deville's graphitoïdal boron) are obtained (1) by fusing aluminium with boric oxide; (2) by fusing aluminium with boric oxide and cryolite, or boric oxide and fluor-spar; and (3) by passing boron fluoride over heated aluminium. Of these processes the first gave the best results, the most important condition for its success being the absence of carbon from the mixture. The temperature of melting iron, maintained for two or three hours, was found sufficient to produce the crystals, but the yield was larger at higher temperatures.

The crystals belong to the monoclinic system. They are black, or, in very thin laminae, dark-red, and yield a brownish-red powder. They have an extremely brilliant lustre, and when heated turn blue like steel, but they are nevertheless unalterable in oxygen at the temperature at which diamond burns easily. They are harder than corundum, but softer than diamond. Their sp. gr. is 2.6346, that of water at 17° being 1. The crystals are not attacked by hydrochloric acid or potash-ley, and only superficially by concentrated sulphuric acid, but are slowly dissolved by nitric acid. They are oxidised with incandescence by fused potash or lead chromate, and slowly dissolved by fused acid potassium sulphate. When heated in the blow-pipe flame on platinum, they form with the metal an easily fusible alloy. Analyses of these crystals prepared at different times gave results agreeing very closely with the formula AlB^{12} .

The yellow crystals (Wöhler and Deville's diamond boron) were obtained by heating aluminium with boric oxide to the highest temperature obtainable in a wind-furnace, in crucibles lined with pure graphite, and allowing the fused mass to cool down very slowly. The crystals are quadratic, the octohedron being the most common form, but sometimes long prisms were obtained. They have a honey-yellow colour, which is a constant characteristic, and is not due, as Wöhler and Deville supposed, to impurities. They are somewhat easily broken, exhibiting a conchoidal fracture, and yield a honey-yellow powder. They are harder than corundum, but softer than diamond. In their behaviour with reagents they closely resemble the black crystals described above. Their sp. gr. is 2.615. The empirical formula of the crystals, as deduced from several closely concordant analyses, is $C^2Al^1B^{12} = CB^{12} + 3AlB^{12}$.

All attempts to obtain pure crystallised boron have hitherto proved fruitless.

Detection.—H. Kämmerer (*Zeitschr. anal. Chem.* 1873, 376) recommends, as a very delicate test for boron, to mix the substance under examination very intimately with fluor-spar and sand in a test-tube, moisten the mixture with strong sulphuric acid, and pass the escaping gases through a glass tube drawn out to a fine point, into the non-luminous flame of a Bunsen burner; the presence of boron will then be revealed by the green coloration of the flame.

According to Bidaud (*Compt. rend.* lxxvi. 409), the flame of a Bunsen burner, directed upon a crystal of boric oxide placed on a piece of porcelain, immediately acquires a splendid green colour. It is not necessary that the crystal should be enveloped by the flame, mere contact with the outer edge being sufficient.

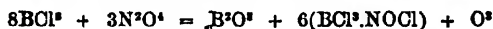
On the spectrum of boric acid vapour, see Lecoq de Boisbaudran (*Compt. rend.* lxxvi. 833).

Boron Chloride, BCl_3 . H. Schmitzler (*Dingl. pol. J.* cxxi. 435) prepares this compound by passing chlorine over a mixture of boric oxide, soot, and oil made up into spherical lumps, and ignited in a porcelain tube, which is connected with a condenser tube 6 inches long and $1\frac{1}{2}$ inch wide, and so inclined that the course of the condensed boric chloride may be opposite to that of the stream of chlorine. This tube lies in a wooden trough, enveloped in snow or pounded ice, over which strong hydrochloric acid is poured from time to time, whereby a temperature of about -10° is produced. By this method about 80 c.c. of boron chloride may be obtained in a few hours.

Reactions.—1. When the vapour of boron chloride, heated to bright redness, is passed through a porcelain tube, either glazed or unglazed, and the substance of the tube is rapidly attacked, the chloride of boron is partially decomposed, chloride of silicon and chloride of aluminium being volatilised, while borate of aluminium remains behind. With a glazed tube, a certain quantity of the double chloride of aluminium and potassium is also formed. Pure alumina, silica, zirconia, and titanica acid ignited in a platinum tube are attacked by boric chloride in a similar manner, except that, in the case of the three latter substances, the residue consists of boric oxide (Troost and Hautefeuille, *Compt. rend.* lxxv. 1819).

2. When *nitrogen tetroxide* is distilled into refrigerated boron chloride, an energetic action takes place, and a solid substance is deposited in the liquid, while yellow crystals condense on the sides of the flask. On leaving the product at rest for two days, and then distilling at a gentle heat, volatile yellow crystals condense in the receiver, giving off a brownish red vapour which fumes on coming in contact with the air. A liquid, apparently consisting of a solution of the crystals in boron chloride, also passes over. The crystals have the composition BCl_3NOCl , and form rhombic octohedrons or prisms which dissolve in water with a hissing sound, boric acid, nitric acid, and chlorine being produced. At 23° – 24° the crystals melt, forming two layers of liquid, the upper of which appears to consist of boron chloride containing a small proportion of the original substance, while the lower probably consists of the fused substance together with a small proportion of nitrosyl chloride. On cooling, the two layers reunite with more or less rapidity, reproducing the original substance.

The reaction by which these crystals are formed is probably as follows:—



(Geuther, *J. pr. Chem.* [2], viii. 854).

Boric Oxide, Acid, and Salts. A description of the method of obtaining boric acid from the Tuscan lagoons is given by C. M. Kurtz (*Dingl. pol. J.* cxxii. 493; *Jahresb. f. Chem.* 1874, 1108); also by P. Le Neve Foster (*Pharm. J. Trans.* [3], v. 343).

Effect of sudden Cooling on Boric Oxide.—The glassy plate produced by pouring fused boric oxide on a cold metallic surface has its lower face in a more dilated condition than its upper face. The consequence is a bending of the plate, which may be so great as to cause it to fly in pieces. Such a plate acts upon polarised light like unannealed glass, but, unlike the latter, it retains this power with extraordinary tenacity. Fragments kept at a red heat for fifteen hours, and then cooled slowly during several days, were found to act on polarised light as strongly as before, while, by the same treatment, blocks of glass weighing 60 kilos. were completely annealed. When boric oxide, which has been suddenly cooled is plunged into water, the portions which are already most dilated do not, in taking up water, undergo so great an increase of volume as those which have cooled more slowly, and a kind of exfoliation occurs by the detachment of successive layers (V. de Luynes, *Compt. rend.* lxxxi. 80).

Hydrates.—When boric acid, BO^+H^- or $\text{B}^+\text{O}^-\cdot 3\text{H}^+\text{O}$, is heated for a week to 100° , it is converted into the hemihydrate, $2\text{B}^+\text{O}^-\cdot \text{H}^+\text{O}$, and if heated for the same time to 140° , into the trito-hydrate, $3\text{B}^+\text{O}^-\cdot \text{H}^+\text{O}$ (Atterberg).

Metallic Borates. Action of Water.—Water does not decompose the borates of the alkali-metals, but readily separates oxides from many metallic borates, which are scarcely altered by contact with concentrated solutions of neutral or acid sodium borate. Hence the reaction between alkaline borates and salts of other metals in very strong solutions gives a pure metallic borate if the alkaline borate is used in excess, and an oxide when the metallic salt is in large excess, this oxide arising from the action of water on the metallic borate first produced (L. Joulin, *Ann. Chim. Phys.* [4], xxx. 248).

The following metallic borates have been examined by Atterberg (*Bull. Soc. Chim.* [2], xxii. 350):—

$2\text{B}^2\text{O}^3.\text{K}^2\text{O} + 5\frac{1}{2}\text{H}^2\text{O}$.	Large hexagonal prisms	$5\text{B}^2\text{O}^3.\text{Na}^2\text{O} + 10\text{H}^2\text{O}$ (?)
$2\text{B}^2\text{O}^3.\text{K}^2\text{O} + 6\text{H}^2\text{O}$.	Short monoclinic prisms	$5\text{B}^2\text{O}^3.(\text{NH}^4)^2\text{O} + 8\text{H}^2\text{O}$.
$5\text{B}^2\text{O}^3.\text{K}^2\text{O} + 8\text{H}^2\text{O}$.	Rhombic octohedrons	$\text{B}^2\text{O}^3.\text{BaO} + 2\text{H}^2\text{O}$. Cryst. powder.
$\text{B}^2\text{O}^3.\text{Na}^2\text{O} + 4\frac{1}{2}\text{H}^2\text{O}$.	Elongated prisms	$\text{B}^2\text{O}^3.\text{BaO} + 4\text{H}^2\text{O}$.
$\text{B}^2\text{O}^3.\text{Na}^2\text{O} + 5\frac{1}{2}\text{H}^2\text{O}$.	Tufts of elongated prisms	$3\text{B}^2\text{O}^3.2\text{BaO} + 6\text{H}^2\text{O}$.
$\text{B}^2\text{O}^3.\text{Na}^2\text{O} + 8\text{H}^2\text{O}$.		$3\text{B}^2\text{O}^3.\text{BaO} + 6\text{H}^2\text{O}$.

The following sodium borates have been examined by R. Benedikt (*Deut. Chem. Ges. Ber.* 1874, 700). The *monobasic* or *metaborate of sodium*, $\text{BO}^2\text{Na} + 4\text{H}^2\text{O}$, which Berzelius obtained by igniting borax with sodium carbonate, is more easily prepared by mixing the solutions of equivalent quantities of borax and pure caustic soda, and evaporating to a syrupy consistence. This concentrated solution left for several days over sulphuric acid, yields large splendidly-developed crystals, often more than an inch long, which may also be obtained by recrystallising the product of the first, often somewhat confused crystallisation: they become dull on the surface when exposed to the air. According to Hahn, these crystals are monoclinic (*1st Suppl.* 360), but from recent measurements by Ditscheiner they appear to belong to the triclinic system.

	001	100	111	111	110	110
or	oP	$\infty\text{P}\infty$	P	P	$\infty\text{P}'$	$\infty'\text{P}$

As Hahn states that the salt which he measured was isomorphous with octohedral borax, $\text{B}^2\text{O}^3.\text{Na}^2 + 5\text{H}^2\text{O}$, it is possible that he may actually have examined only the last-mentioned salt.

If in the above-described preparation of the metaborate a large excess of sodium hydrate be added, the process being otherwise conducted as before, large fine needles are formed, which, when freed from mother-liquor by decantation, quickly rinsed with water, and dried on a plate under the air-pump, retain their lustre only so long as they are protected from the air. Their analysis leads to the formula $\text{BO}^2\text{Na} + 2\text{H}^2\text{O}$. The same hydrate is formed by fusing the salt, $\text{BO}^2\text{Na} + 4\text{H}^2\text{O}$, in its water of crystallisation. According to Berzelius, the salt thus produced has the composition, $\text{BO}^2\text{Na} + 3\text{H}^2\text{O}$.

By fusing either of these hydrates of sodium borate with an equivalent quantity of barium chloride in a platinum crucible, and lixiviating the fused mass with water, the salt, $\text{B}^2\text{O}^3.\text{Ba}$ or $\text{BaO}.\text{B}^2\text{O}^3$, is produced. The corresponding calcium and strontium salts may be formed in the same way.

When either of the sodium salts is fused with the quantity of sodium hydrate required by the equation



water is rapidly given off, and on cooling there remains a beautiful laminar hard crystalline cake, which, when dissolved in water, again yields the metaborate, $\text{BO}^2\text{Na} + 2\text{H}^2\text{O}$. It does not indeed appear possible to obtain in this way the orthoborate of sodium, BO^2Na^* . In fact, the only orthoborate yet obtained is the magnesium salt, $(\text{BO}^2)^2\text{Mg}^2$ (i. 644).

Sodium Biborate. Borax, $\text{Na}^2\text{B}^2\text{O}^7 + 10\text{H}^2\text{O} = \text{Na}^2\text{O}.2\text{B}^2\text{O}^3 + 10\text{H}^2\text{O}$, has been found in large quantity in the bed of a dried-up lake 140 miles north-west of Bakersfield, in the Sierra Nevada. The bed is 15 miles long and 6 miles broad, and the saline deposits are from 6 to 8 feet deep. The middle of these deposits consists of common salt, the borax occupying the edges to a depth of 3 feet. Beneath the pure borax is a deposit of sodium sulphate and tincal (*A. Robottom, Chem. News, xxii. 286*).

According to C. F. Schultze (*Arch. Pharm.* [3], vi. 149), borax dissolves abundantly in glycerin, 1 part of glycerin taking up an equal weight of it. The solution is capable of taking up cream of tartar.

Iodine dissolves in a dilute solution of borax, with formation of sodium iodide and iodate, but separates out when the solution is concentrated. This fact, observed by Bottomley (*Chem. News, xxi. 76*), is attributed by him to a resolution of the borax in the dilute solution into soda and boric acid, whilst latter, on concentration, sets free the hydriodic and iodic acids, which then decompose one another with liberation of iodine.

Octohedral Borax.—A strongly supersaturated solution of borax (e.g. 2 parts water to about 1.5 borax), protected from the falling in of borax powder, deposits crystals of octohedral borax, $\text{Na}^2\text{B}^2\text{O}^7 + 6\text{H}^2\text{O}$; but, if the supernatant liquid be touched with a crystal of ordinary prismatic borax, it will immediately deposit crystals of the latter. Octohedral crystals likewise form in a solution of borax evaporated under the air-pump.

On the Antiseptic action of Borax and Boric acid, see FERMENTATION.

Preparation of Crystalline Borates in the dry way.—Great difficulty has hitherto been experienced in preparing crystalline borates in the dry way, on account of their ready fusibility: hence they have hitherto been obtained in this manner only as amorphous vitreous masses. A. Ditté (*Compt. rend.* lxxvii. 783, 892), has, however, overcome the difficulty by adding the borate to be crystallised, or its constituents, to a mixture of alkaline chlorides in equivalent proportions contained in a platinum crucible, so arranged over the lamp that the bottom only is at a red heat. The borate sinks and dissolves in the chlorides, which are but just in a state of fusion on the surface. On reaching the surface again by convection, the borate becomes crystalline. It is easily detached from the cooled mass, and is then washed with hot water.

Calcium Borates.—A saturated boiling solution of boric acid readily attacks Iceland spar, marble, chalk, or dolomite, forming small needles. These crystals present the same appearance as the crusts of natural calcium borate which are found in Tuscany on the limestone, and which Beudant supposed were formed by the action of borax upon the carbonate. The composition of the borate formed by the action of boric acid on a carbonate is expressed by the formula $\text{Ca}^2\text{H}^2\text{B}^4\text{O}^8 \cdot (\text{H}^2\text{BO}^3)^2$, or monocalcic tetrametaborate, plus 2 mols. of boric acid. This compound loses its water at 200° , and fuses at 450° . When it is introduced into the crucible containing the alkaline mixture, kept at as low a heat as is compatible with fusion, the crystals which form on the surface have the following composition:—Lime = 44.5%, boric oxide = 55.42, corresponding with the formula $\text{Ca}^2\text{B}^4\text{O}^8$, or calcium metaborate. The same result is obtained with the precipitate—a sesquimetaborate, according to Rose—which is formed on adding borax to a soluble calcium salt. The addition of a small quantity of calcium chloride to the fused mass in the above experiments causes crystallisation to take place more quickly, but with no alteration in composition. The crystalline borate appears in the form of four-sided prisms, often flattened out into plates, and arranged in fluted masses. It is colourless, transparent, very fusible, readily soluble at 50° in concentrated hydrochloric or nitric acid diluted with its own bulk of water, but insoluble in boiling concentrated acetic acid. If the calcium chloride employed in hastening the formation of the crystals amounts to a fourth of the whole mixture, a borate is crystallised having the formula $\text{Ca}^3\text{B}^4\text{O}^8 (= \text{Ca}^2\text{B}^4\text{O}^8 + \text{B}^2\text{O}^3)$, or calcium orthoborate plus one mol. of boric oxide. This is also formed when a little boric acid is added to a fusing mixture of 2 parts of potassium chloride, 2 parts of sodium chloride, and 1 part of calcium chloride. The crystals have the form of long prisms, striated parallel to the side-edges. They are soluble in all acids except acetic. The third crystalline calcium borate formed has the composition, lime = 34.67, boric oxide = 65.32, corresponding with the formula $\text{Ca}^2\text{B}^3\text{O}^{11} (= \text{Ca}^2\text{B}^4\text{O}^8 \cdot \text{B}^2\text{O}^3)$, or 2 mols. of calcium metaborate, plus 1 mol. of boric oxide. It is obtained by adding to the mixed chlorides in fusion, precipitated calcium borate, or the product of the reaction of boiling boric acid solution on calc-spar, with the addition of one-third its weight of fused boric acid. The crystals are long, silky, slender needles. The same salt is obtained in flattened pearly needles, when boric acid is simply fused with chalk. If, in the former operation, the boric acid, instead of being one-third of the weight of the borate employed, be in great excess, the crystallisation is retarded, and the salt formed, which is in flat needles soluble in cold nitric acid, is the calcium analogue of borax.

Strontium Borates.—Strontium carbonate behaves like calcium carbonate with a boiling solution of boric acid. But if the product of the reaction, or the precipitate produced by mixing borax with a soluble strontium salt, be added to the heated chlorides, it does not fuse, but is converted into strontium borax, containing strontia = 42.66, boric oxide = 57.33, corresponding with the formula SrB^4O^7 . Even when a slight excess of strontium chloride is present, the same result is obtained. If in the last case a jet of steam be directed upon the top of the melting contents of the crucible, crystals are formed which do not differ in composition from those last mentioned. This compound forms long needles soluble in cold nitric acid. If caustic strontia be added in excess in either of the last three experiments, opaque striated four-sided prisms crystallise out. These are very soluble in acids, and have the composition $\text{Sr}^2\text{B}^4\text{O}^{11}$. When one equivalent of boric acid and one equivalent of caustic strontia are heated strongly in a carbon crucible, brilliant needles are obtained, which, when added to the mixture of heated chlorides containing a little strontium chloride, are converted into short striated crystals consisting of SrB^4O^7 . If, in the last operation, caustic strontia be also added in excess, small flat prisms are obtained. They are coloured yellow by a trace of iron, and have the composition $\text{Sr}^2\text{B}^4\text{O}^8$. This compound dissolves in all dilute acids except acetic.

Barium Borates.—When the precipitate formed by adding borax to a soluble barium salt is dissolved in the fused chlorides, needles are obtained which show a

tendency to group themselves in crosses or stars, the branches of which are inclined to each other at an angle of 60° . The composition of these crystals is barium 52.37, boric oxide 47.63, corresponding with the formula $\text{Ba}^2\text{B}^2\text{O}^7$. Boric oxide and caustic baryta, when brought to a strong red heat in equivalent quantities, in a carbon crucible, yield a grey crystalline mass, which, when submitted to the action of the mixed chlorides, with addition of barium chloride, furnishes white six-sided prisms terminated by pyramids. They are readily soluble in warm dilute acids, and contain barium 58.46, boric oxide 41.54, corresponding with the formula $\text{Ba}^2\text{B}^2\text{O}^{11}$.

Magnesium Borates.—When a mixture of magnesia and boric oxide, the latter in large excess, is brought to a white heat in a carbon crucible, hard, white opaque masses are left on cooling, surrounded by the glass of boric acid. These masses consist of long needles radiating from centres. They are soluble in all warm dilute acids, except acetic, and contain magnesia 30.00, boric oxide 70.00, corresponding with the formula $\text{Mg}^3\text{B}^2\text{O}^{14}$ ($= 3\text{MgB}^2\text{O}^4 \cdot \text{B}^2\text{O}^3$), which is the formula of the boracite from Lunenburg. When this compound is introduced into the fused chlorides, it loses half its boric oxide, the liberated oxide forming transparent drops attached to the portions of salt which are yet unaltered. The crystals which form are large, transparent, flattened needles, terminated by points. They dissolve in warm dilute nitric and sulphuric acid, and contain magnesia 46.40, boric oxide 53.60, corresponding with the formula $\text{Mg}^2\text{B}^2\text{O}^6$. The same compound is produced if the operation is commenced with one equivalent of magnesia and two equivalents of boric oxide. If the artificial boracite be heated very strongly with the mixed chlorides, it loses a fourth only of its boric oxide. The crystals thus obtained are in the form of needles or of prisms, which contain magnesia 36.85, boric oxide 63.15, corresponding with the formula MgB^2O^4 .

The constitution of the borates of barium, strontium, and magnesium above described is similar to that of the analogous calcium compounds.

Double Borates.—If the artificial boracite be heated in the mixed chlorides with a large excess of calcium chloride, the crystals form very slowly, and the salt is obtained in prisms terminated by regular pyramids. It contains lime 29.78, magnesia 21.24, boric oxide 48.87, corresponding with the formula $\text{Ca}^2\text{Mg}^2\text{B}^2\text{O}^{18}$ [or $\text{Ca}^2\text{B}^2\text{O}^6 \cdot \text{Mg}^2\text{B}^2\text{O}^6$]. If strontium chloride be substituted for the calcium chloride, the compound MgB^2O^4 is alone obtained. But if caustic strontia be substituted, a double salt of strontium and magnesium, exactly analogous to the magnesio-calcic salt described above, is produced, containing strontia 43.60, magnesia 16.40, boric oxide 40.00. Both these double salts dissolve easily in dilute acids.

Estimation of Boric acid.—The following method, depending on the conversion of the boric acid into crystallised calcium borate, is recommended by A. Ditte (*Compt. rend.*, lxxx. 490, 561) as easier and more exact than any of the processes commonly employed.

When the boric acid is combined only with alkalis, the solution, neutralised if necessary with ammonia, is mixed with excess of a saturated solution of pure calcium chloride, which throws down a gelatinous precipitate of uncertain composition, soluble in excess of calcium chloride. The mixture is evaporated to dryness in a platinum crucible, which is then filled up with a mixture in equivalent proportions of the pure chlorides of potassium and sodium, and the whole is heated, gently at first, over a gas-jet, so as to fuse the mixed chlorides. Calcium borate, CaB^2O^4 , in the form of a spongy mass, settles down, is partly dissolved, and then forms a ring of crystals which rises as a crown in the upper and cooler part of the crucible. The mass removed from the crucible is treated with water and washed on a filter, and the crystalline needles of calcium borate are brushed off and weighed.

The essential precautions are not to fuse the spongy mass first formed, but otherwise to keep the bottom of the crucible as hot as possible, while the sides and upper part are kept as cool as possible, consistent with the fluidity of the mixed chlorides.

If the borate is insoluble in water, and contains bases other than alkalis, it is dissolved in dilute hydrochloric acid, and the bases are separated by the usual method, care being taken not to introduce any substances capable of forming an insoluble salt with calcium chloride. If, therefore, alkaline carbonates have been used to precipitate the bases, they must be decomposed by hydrochloric acid, and the solution heated gently so as to expel the carbonic acid without volatilising any of the boric acid. The liquid is then to be treated with ammonia, calcium chloride added in excess, and the process continued in the manner above described.

The same method is applicable to the estimation of the boric acid which occurs in several silicates. If the mineral is easily decomposable by acids, as is the case with datholite and botryolite, it is finely pulverised, and decomposed by digestion for

several hours with hydrochloric acid at 50° – 60° , and a saturated solution of calcium chloride is added, together with ammonia to neutralise the free acids. The boric and silicic acids are thereby converted into calcium salts, and the liquid may be evaporated to dryness without loss of boric acid. The whole is then introduced into a crucible and gradually heated to fusion, whereupon the greater part of the calcium borate crystallises in a ring at the surface, while the silicate remains at the bottom. After cooling the ring of borate is detached, and the remainder remelted, in order to crystallise the small residual portion of borate; then after a few minutes the bottom of the crucible is heated as strongly as possible, to frit and agglomerate the silicate of calcium. On treating the ring and the cooled mass with cold water to remove soluble salts, the whole of the boric acid remains in the form of crystallised calcium borate, mixed with silicate, in the form of small semi-fused grains or sometimes small crystals. The whole is easily washed, and may be weighed after drying.

To complete the estimation, the mixture of borate and silicate of calcium is heated with nitric acid, the whole evaporated to dryness, and the residue digested with solution of ammonium nitrate, whereby the lime is completely dissolved out, and may be estimated in the solution. The residue, after washing and calcination, consists of pure silica, which may then be weighed. The weights of the lime and silica deducted from that of the mixture of borate and silicate give the weight of boric oxide, B_2O_3 , in the original compound.

If the substance to be analysed is not easily attacked by acids, it is calcined with excess of potassium or sodium carbonate, and the calcined mass is treated with hot water containing a little sal-ammoniac: the liquid is evaporated to dryness, and the residue is digested with water, which leaves the insoluble bases together with a portion of the silica, the filtered liquid containing the rest of the silica, together with the whole of the boric acid. This filtrate is treated with hydrochloric acid to decompose the excess of alkaline carbonates; the whole is heated to expel carbonic acid; ammonia and calcium chloride are added; the solution is evaporated to dryness; and the analysis completed as above.

To analyse a compound or mixture of borates and fluorides, the solution of the substance in hydrochloric acid is treated with calcium chloride and ammonia as above, the whole evaporated to dryness, and the mixture of alkaline chlorides and calcium borate and fluoride is heated, whereby the calcium fluoride, which when first precipitated is gelatinous and very difficult to wash, is rendered compact and dense, so that, when the contents of the crucible are treated with cold water, the mixture of calcium borate and fluoride is easily loosened, and may then be washed, dried, and weighed. The mixed salts are next treated with a hot strong solution of ammonium nitrate, which completely dissolves the borate and leaves the fluorides. This latter is finally washed and weighed, and its weight deducted from that of the whole gives the weight of the borate.

Finally, whether the salt to be analysed is a simple borate or a mixture of a borate with silicate or fluoride, the boric acid may always be estimated in the form of calcium borate, and the same method may be applied in nearly all cases of the estimation of boric acid (A. Ditte, *Compt. rend.* lxxx. 563).

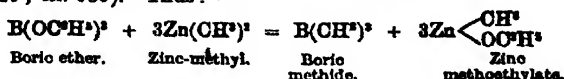
Fluoboric acid.—According to A. Basarow (*Bull. Soc. Chim.* [2], xxii. 8), the so-called fluoboric acid, $HBO_2 \cdot 3HF$, discovered by Gay-Lussac and Thénard, and examined by S. Davy and Berzelius (i. 663), has no existence. When water is saturated with gaseous boron fluoride and the liquid is subjected to fractional distillation in a platinum retort heated in an oil-bath, products are obtained, differing in specific gravity and composition, according to the temperatures at which they distil. 1 c.c. of water at 0° and 762 mm. pressure absorbs 1057 c.c. of boron fluoride.

The *fluoborates*, usually described as definite salts, appear also to have been nothing but mixtures. Thus the sodium salt, $NaBO_2 \cdot 3NaF + 4H_2O$, described by Berzelius, is resolved by fractional crystallisation into sodium fluoride, neutral sodium borate, borax, and a translucent gelatinous mass which is insoluble in water, and dries up to a white crystalline powder. Neither is it possible to obtain a definite fluoborate of silver. A solution of $NaBO_2 + 3NaF$ gives with silver nitrate the characteristic reaction of the borates—that is to say, a partly white, partly brown precipitate of silver borate and oxide. The attempt to prepare a fluoboric ether was likewise unsuccessful. It may therefore be concluded that neither fluoboric acid nor its salts have any existence (*Deut. Chem. Ges. Ber.* vii. 1121).

BORON, ORGANIC COMPOUNDS OF. *Triallylic Borate*, or *Boric Triallylate*, $B(OC^3H^7)^3$. This ether is formed in small quantity when boron chloride is passed into absolute allyl alcohol, and more abundantly when a mixture of boric oxide and allyl alcohol is heated to 130° in sealed tubes. The product is a colourless mobile liquid having a tear-exciting odour, and boiling between 168° and 175° . It

burns with a green flame, and is constantly decomposed by water, with separation of boric acid (O. Counciler, *Dent. Chem. Ges. Ber.* ix. 485).

Derivatives of Triethylic Borate.—Frankland, in 1862, described the action of zinc-ethyl and zinc-methyl on triethylic borate, and showed that these organo-metallic bodies displace the ethoxyl (OC^2H^5) by the organic radicle which they contain (ii. 525; iii. 985). Thus:—

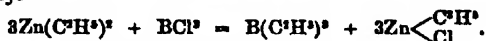


Further, that boric ethide, when cautiously exposed to a slow current, first of air and then of dry oxygen, takes up 2 at. oxygen, forming boric etho-diethylate, $(\text{C}^2\text{H}^5)_2\text{B}(\text{OC}^2\text{H}^5)^2$, a liquid boiling with partial decomposition between 95° and 125° , but distilling unchanged under reduced pressure. By contact with water this compound is easily changed into boric ethodihydrate, $(\text{C}^2\text{H}^5)_2\text{B}(\text{OH})^2$. Thus:—

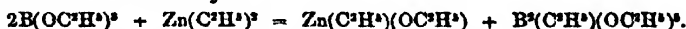


Further experiments by Frankland (*Proc. Roy. Soc.* xxv. 165) have led to the following results:—

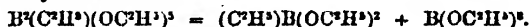
Boric ethide may be prepared by passing a current of the vapour of boric chloride through zinc-ethyl—



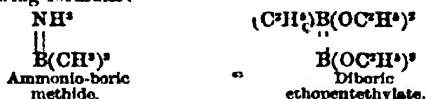
Boric ethopentethylate, $\text{B}^2(\text{C}^2\text{H}^5)(\text{OC}^2\text{H}^5)^3$, is formed by heating 2 mols. of boric ether with 1 mol. of zinc-ethyl—



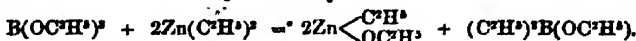
It is a colourless, mobile liquid, boiling at about 112° , and condensing without alteration. Its vapour-density, taken between 114° and 120° , is 80 ($\text{H}=1$), which represents a 4-volume condensation, indicating that the compound, in passing from the liquid to the gaseous state, is broken up into boric ethodihydrate and boric triethylate—or triethylic borate—



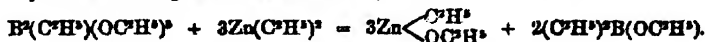
A similar deportment is exhibited by ammonio-boric methide, $\text{NH}^3\text{B}(\text{CH}^3)^3$, which is resolved by heat into NH^3 and $\text{B}(\text{CH}^3)^3$, the mixed vapour resulting from the decomposition having also a 4-volume condensation. These decompositions, which are similar to that of sal-ammoniac, NH^4Cl , into NH^3 and HCl , together occupying 4 vols. of vapour, render it probable that the compounds under consideration have a constitution analogous to that of the ammonium-salts, and that boron, though usually triadic, may, like nitrogen, enter into combination as a pentad. On this view the constitution of ammonio-boric methide and diboric ethopentethylate may be represented by the following formulæ:



Boric dietho-ethylate, $(\text{C}^2\text{H}^5)^2\text{B}(\text{OC}^2\text{H}^5)$, intermediate between boric ethide and boric ethodihydrate, is formed in large quantity by boiling boric ether with 2 mols. of zinc-ethyl:



When thus prepared it retains a small quantity of boric ethylate or of diboric ethopentethylate, from which it cannot be freed even by repeated rectification. It may, however, be obtained pure by distilling diboric ethopentethylate with 3 mols. of zinc-ethyl, in an atmosphere of carbonic anhydride:

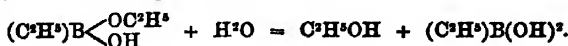


This product, when rectified, is a colourless, mobile liquid, having an ethereal odour and pungent taste, boiling at 102° , distilling unchanged, and having (at 135.5°) a vapour-density of 56.5 ($\text{H}=1$), indicating a normal 2-volume condensation. It takes fire in the air and burns with a greenish flame. Exposed to dry air, and then to oxygen, it oxidises to boric ethodihydrate:



Boric diethohydrate, $(C^2H^5)_2B(OH)_2$, formed by agitating boric diethoethylate with water, is a spontaneously inflammable ethereal liquid, which resembles boric ethide and is decomposed on distillation.

Boric etho-ethylate hydrate, $(C^2H^5)_2B \begin{smallmatrix} OC^2H^5 \\ OH \end{smallmatrix}$, is formed by exposing boric diethohydrate in a cooled vessel to a slow current of dry air. It is liquid at ordinary temperatures, but solidifies below 8° to a white crystalline body, smelling like boric ethide, and having a pungent taste. It is rapidly decomposed by water into alcohol and boric ethodihydrate, according to the equation:



It is not spontaneously inflammable, and cannot be distilled under ordinary atmospheric pressure without decomposition.

BOURNONITE. A finely crystallised specimen of this mineral from the Herod's Foot mine at Liskeard, in Cornwall, having a specific gravity of 5.826, has been analysed by C. E. Wait (*Chem. News*, xxviii. 271), with the following result:

S	As	Sb	Pb	Cu	Fe
19.359	0.469	23.677	41.949	13.268	0.679 = 99.301.

On the Crystalline forms (ortho-rhombic) of Bournonite from Waldenstein in Carinthia and Příbram in Bohemia, see v. Zepharovich (*Jahrb. f. Min.* 1878, 555; *Chem. Soc. J.* 1877, i. 583).

See BERTHOLLETTIA (p. 322).

BRAZILIN and BRAZILINUM. Brazilin, the colourless crystalline substance which is extracted from Brazil-wood, and turns red when exposed to the air in contact with alkalis, has, according to E. Kopp, the composition $C^{22}H^{10}O^7$ (2nd Suppl. 208). According to Liebermann a. Burg, on the other hand (*Deut. Chem. Ges. Ber.* x. 1883), its composition is $C^{16}H^{14}O^6$, and it gives with lead acetate a white precipitate, $C^{16}H^{14}PbO^6 + H^2O$, which becomes rose-coloured when dry, gives off its water at 130° , and then becomes darker.

Acetyl-brazilin, $C^{16}H^{10}(C^2H^3O)^4O^6$, is obtained by heating brazilin to 130° with acetic anhydride, and when purified by recrystallisation from alcohol, forms white anhydrous needles having a satiny lustre, and melting at 149° – 151° .

Chloro-brazilin, $C^{16}H^{12}Cl^2O^6$, and *Bromo-brazilin*, $C^{16}H^{12}Br^2O^6$, are obtained by treating the aqueous solution of brazilin with chlorine- and bromine-water.

If these results are correct, hæmatoxylin, $C^{16}H^{14}O^6$, the colouring matter of log-wood, is simply oxybrazilin, and is related to brazilin in the same manner as purpurin to alizarin. According to E. Kopp's formula, on the other hand, brazilin is related to hæmatoxylin and resorcin in the manner represented by the equation:



and it appears from Kopp's experiments that resorcin is actually obtained by the dry distillation of brazilin.

Brazilein, the red colouring matter produced by oxidation of brazilin in contact with alkalis, has, according to Liebermann a. Burg, the composition $C^{16}H^{12}O^6$, being formed from brazilin by abstraction of 2 at. hydrogen. The product formed in the first instance is a salt, from which the brazilein may be separated by acids, in the form of an amorphous violet precipitate, which acquires a fine gold colour when dry. Crystallised brazilein may be obtained by treating a hot aqueous solution of brazilin with an alcoholic solution of iodine. The crystals are grey, silvery, rhombic plates, which dissolve in alkalis, forming a purple-red solution from which the brazilein is reprecipitated by acids.

Another red colouring matter (also called brazilein) is formed from brazilin by the action of nitrous acid (Reim, *Deut. Chem. Ges. Ber.* iv. 333), also by oxidation in the air, in contact with ammonia, the ammonia being doubtless first oxidised to nitrous acid, which then acts on the brazilin as above. The colouring matter thus produced contains nitrogen, and when purified by solution in potash, precipitation with hydrochloric acid, and drying at 125° , has the composition $C^{16}H^{11}NO^6$ or $N(C^{16}H^{11}O^6)$.

Adopting Kopp's formula for brazilin, the formation of the nitrogenous colouring matter may be represented by the equation:



It is related to brasilin, $\text{C}^{\text{As}}\text{H}^{\text{As}}\text{O}^{\text{As}}$, in the same manner as hematite to hematopyllid and phlorein to phloroglucin (R. Benedikt, *Liebig's Annalen*, clxxx. 100).

BREAD. Respecting the Detection and Estimation of Alum in Bread, see ALUM (p. 67).

See ELEM.

An amorphous arsenical variety of this mineral (i. 316) called Arite, occurring, together with galena, blende, ullmanite and quartz, on the Ar mountain at the foot of the Pic de Ger, near Eaux-Bonnes, Dep. Basses Pyrénées, has been analysed by F. Pisani (*Compt. rend.* lxxvi. 239) with the following results:—

S	As	Sb	Ni	Zn	Sp. gr.
1.7	11.5	48.6	37.3	2.4	101.5

These numbers lead to the formula $\text{Ni}(\text{Sb}, \text{As})$.

BRITTLE SILVER ORN. See STEPHANITE.

BROCHANTITE GROUP OF MINERALS (A. Schrauf, *Jahrb. f. Min.* 1873, 959). The minerals of this group are isomorphous with malachite. Monoclinic (approximately). Axial ratio $a : b : c = 0.7797 : 1 : 0.4838$. Angle $b : c = 90^\circ 32'$. The more exact measurements of brochantite cannot be referred to Koksharov's rhombic system of axes (*Jahresb. f. Chem.* 1860, 785); and, indeed, the measurements of the pyramids of brochantite of Rezanya give values which point to the triclinic system. Twin-formation is predominant, as in the plagioclases. The following types of brochantite have been examined by Schrauf:—

Type I.—Brochantite from Rezanya. Triclinic. Axial system, $a : b : c = 0.810344 : 1 : 0.494643$. There is a blackish-green variety not yet analysed, and a light-green variety containing 65.69 p.c. CuO and 17.5 SO^2 . To this type belong also the brochantites from Redruth in Cornwall, and of Gumeschewsk and Nischne-Tagilsk in the Ural. There are also indistinctly crystallised varieties ($7\text{CuO} \cdot 2\text{SO}^2 \cdot 6\text{H}^2\text{O}$) from several localities, viz., from Nassau; from Iceland (krisuvigite); Chile, Atacama, Mexico (brogniartite); Arizona, New South Wales, and Cumberland; from Neu-Moldova, Orawicza and Russ-Kitza in Hungary; from Sanaka in the Banat; from Salzburg; from Zellerfeld in the Hartz; and from Illobo in Hungary.

Type II.—Waringtonite from Cornwall ($3\text{CuH}^2\text{O}^2 \cdot \text{CuSO}^4 \cdot \text{H}^2\text{O}$). Third variety from Rezanya. Monoclinic?

Type III.—From Nischne-Tagilsk: not analysed. Monoclinic-triclinic.

Type IV.—'Königinn' from Russia. Fourth variety from Rezanya, $3\text{CuH}^2\text{O}^2 \cdot \text{CuSO}^4$. Monoclinic or rhombic?

BROMAL, $\text{CBr}^3 \cdot \text{CHO}$. On the formation of this compound, and its combination with hydrocyanic acid, see p. 58 of this volume. On its reaction with *Benzene*, see p. 159.

When bromal is treated with potassium cyanide and alcohol, a large quantity of hydrogen cyanide is given off, and on addition of water, ethylic dibromacetate, $\text{CHBr}^2 \cdot \text{CO}^2 \cdot \text{C}^2\text{H}^5$, separates as a heavy oil, boiling without decomposition at $192^\circ\text{--}195^\circ$ (N. Remi, *Deut. Chem. Ges. Ber.* viii. 695).

BROMELIACEÆ. The micrographic and chemical characters of the textile fibres of certain plants of this order have been examined by Schlesinger (*J. Pharm. Chim.* [4], xviii. 161). The fibres of *Billbergia Leopoldi* are simple and regular in form; their walls are parallel, and everywhere of the same thickness. A cavity, which is nearly always less than half the diameter of the cellule, is always present. The diameter of the fibres is small, varying from 6 to 13 millimeters, and their length is considerable, so that they are specially suitable for fine tissues. When acted upon by freshly prepared ammoniacal oxide of copper, the fibres undergo a curious change. Some of them swell out and turn round their own axis, forming ringlets and knots; others puff out in an undulatory manner, and, under the prolonged influence of the reagent, lose all their cellular membranes, while their internal membranes are decom-

acid slightly decomposes them. A solution of caustic soda readily isolates the fibres.

In *Macrochordium Tinctorum* the fibres have a maximum diameter of about 14 millimeters, and the length of the cellulose is very small, varying from 2 to 6 millimeters. The ends of the cellulose are rather blunt, rarely pointed. As the fibres have not very thick walls, the cavity is large and sometimes occupies half the diameter of the cellulose; this, however, is irregular, and gives to all the fibre an irregular form.

Ammoniacal oxide of copper causes a great swelling of the fibre, without, however, changing its form; concentrated sulphuric acid dissolves it completely; nitric acid colours it yellow; and a solution of caustic soda causes the walls to swell, so that the cavity is reduced to a small line, and sometimes disappears altogether.

Bromide of Hydrogen, Hydrobromic acid.—The direct formation of this compound from its elements may be strikingly exhibited by setting fire to hydrogen gas which has passed over bromine; thick fumes of hydrobromic acid being thereby produced (Merz & Weith, *Deut. Chem. Ges. Ber.* vi. 1518).

On the Heat evolved in the solution of Hydrogen Bromide in water, see *2nd Suppl.* 634.—On the Constitution of Aqueous Hydrobromic Acid, and on the reciprocal displacement of Hydrobromic, Hydrochloric, and Hydriodic acids, *ibid.* 653.

On the Heat developed in the action of Hydrobromic acid with the Oxides of Potassium, Mercury, and Silver, and in the decomposition by Water of certain Acid Bromides belonging to the Fatty Series; see the article *HEAT* in this volume.

On the occurrence of Bromine in Apatite, see *2nd Suppl.* 100.

On the Affinity of Bromine for Hydrogen and Oxygen, as measured by the Heat of Combination, *ibid.* 606, 611, 612.

Impurities in Commercial Bromine.—According to Phipson (*Chem. News*, xxviii. 51), commercial bromine sometimes contains cyanogen, which may be detected by gradually adding to the bromine an equal weight of iron filings mixed with 5 pts. of water, filtering rapidly, and leaving the liquid at rest. The whole of the cyanogen is then deposited in a few days as ferriocyanide of iron. This reaction might be employed in testing with pure bromine for cyanogen in steel.

Bromoform, a frequent impurity in bromine, may be detected: (1.) By the quantity of real bromine in saturated bromine-water prepared from the sample coming out too low. (2.) By the characteristic odour of bromoform, which comes out with peculiar distinctness when the bromine is added to a solution of potassium iodide, and the separated iodine is decolorised with sodium thiosulphate (Reymann, *Deut. Chem. Ges. Ber.* viii. 790).

On a Compound of Bromine with Acetic acid and Hydrobromic acid, see *ACETIC ACID* (p. 10).

On the Detection and Estimation of Bromine (*2nd Suppl.* 210, 675); see also *HAZARDOUS* in this volume.

On the use of Bromine in Hydrometallurgy, Assaying and Chemical Technology, see R. Wagner (*Dingl. pol. J.* cccviii. 251; cccix. 544; *Chem. Soc. J.* 1878, i. 741, ii. 214).

Reaction of Bromine with Hydrogen Sulphide.—Dry sulphuretted hydrogen is decomposed by dry liquid bromine into hydrobromic acid gas and clear brown liquid sulphur bromide. This liquid, after the deposition of the sulphur, was found to contain—

While still saturated with HBr	77 per cent. of bromine
After standing two days over lime	66 "
After several months	61 "

Sulphuretted hydrogen acts very slowly on this liquid sulphur bromide, and finally produces a dark yellow solid mass, containing 18 per cent. of bromine saturated with HBr; after standing for one day over lime (during which sulphur bromide escaped by sublimation), it contained 9.6 per cent. of bromine.

The action of sulphuretted hydrogen on bromine dissolved in water is unlimited. After the liquid is saturated at the ordinary temperature with hydrobromic acid, the latter escapes in the gaseous state as fast as it is formed, the rate depending on that at which the stream of hydrogen sulphide is passed through the liquid. The aqueous solution formed at ordinary temperatures contained in a cubic centimeter—

I. After the first violent reaction	1.06 gram of HBr
II. After the addition of bromine, and when the solution had become colourless	1.11 "
III. After further addition of bromine, and when again colourless	1.13 "
In the last case 1 cubic centimeter at 20° weighed 1.762 grams, and contained—	
Water	0.58 gram.
Hydrobromic acid	1.13 " = 64 per cent.
Sulphuric acid	0.052 "

The sulphur bromide from below the liquid in III contained, when dry, 60 per cent. of bromine; after washing with water and standing for several days over lime and sulphuric acid, 56 per cent. of bromine.

A continual stream of hydrobromic acid gas and a concentrated solution of the gas may therefore easily be prepared by passing sulphuretted hydrogen into a solution of bromine in water, till the water is saturated with hydrobromic acid gas; on further addition of sulphuretted hydrogen, the hydrobromic acid gas escapes, and may be absorbed by water in a receiver. The sulphur bromide may be decomposed by hot water, and the solution used again in the next operation to dissolve the bromine. The only drawback in the preparation of hydrobromic acid in this way is the formation of traces of sulphuric acid from the sulphur bromide.

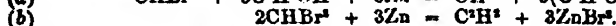
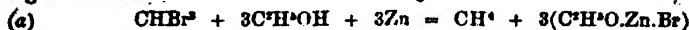
Berthelot supposed that the limited action of sulphuretted hydrogen on iodine in presence of water is due to the formation of a definite hydrate, $HI + 4H^2O$; but, according to the experiments of Thomsen and others, no such hydrate exists at ordinary temperatures (A. Naumann, *Deut. Chem. Ges. Ber.* ix, 1574).

Bromine Chloride, $BrCl$. According to Bornemann (*Liebig's Annalen*, cxxxix, 306), this compound is a red-brown liquid, stable only at temperatures below $+10^\circ$. The hydrate, $BrCl + 5H^2O$, described by Löwig, does not exist; the crystalline mass formed by the action of water on bromine chloride, if indeed a definite compound, has the composition $BrCl + 10H^2O$.

Perbromic acid, BrO^4H , is formed by agitating bromine with aqueous perchloric acid. The potassium salt obtained by neutralisation is isomorphous with the corresponding periodate and perchlorate. The barium salt is formed by mixing the aqueous solutions of potassium perbromate and barium chloride, and separates in crystals on addition of alcohol (Muir, *Chem. Soc. J.* 1874, 324).

$CHBr^3$. This compound may be prepared (like iodoform *q.v.*) by the action of an alcoholic solution of iodine containing phenol on white precipitate (O. Rice, *Chem. Centr.* 1876, 468). According to E. Schmidt (*Deut. Chem. Ges. Ber.* x, 193) its sp. gr. at 14.5 is 2.775 .

Decomposition by the Copper-zinc Couple.—When bromoform in presence of alcohol is brought in contact with a couple having the copper in a finely divided state, reaction takes place in a minute or two, with almost explosive violence. With a coarse couple, a mixture of acetylene and methane is given off, bromethylate of zinc remaining in the flask:



The ratio of acetylene to marsh-gas tends to show that nearly two-thirds of the bromoform is decomposed according to the reaction *a*, the remaining third according to *b*. A considerable quantity of the acetylene produced enters into combination as acetylide of copper.

With zinc-foil in presence of alcohol, a temperature of 60° is required to start the reaction, which then goes on rapidly, yielding also marsh-gas and acetylene, but the marsh-gas is in much larger proportion than when the couple is used, and the whole of the acetylene formed is evolved as gas.

In presence of water, the couple acts very slowly on bromoform at ordinary temperatures; with evolution of marsh-gas and formation of zinc bromide and oxybromide. At 60° the action is more rapid, and a little acetylene is evolved, together with the marsh-gas (Gladstone & Tribe, *Chem. Soc. J.* [2], xiii, 510).

On the Detection of Bromoform in Commercial Bromine, see p. 350.

BROMOXAFORM. This body, which Cahours obtained by the action of bromine on potassium citrate and on dibromocitraconic acid, has been regarded by Cloes and by Lagermark as pentabromomethyl acetate, $CBBr^5.O^4HBBr^2O^2$. Cloes, in fact, states that it can be formed by simply pouring bromine on methyl acetate; and, according

to Steiner, it is formed by the action of bromine on this ether at 150°. Grimaux, on the other hand (*Compt. rend.* lxxviii. 1442), finds that bromine may be left in contact with methyl acetate for a month without the slightest action, and that at 150° a reaction takes place, resulting in the formation of methyl bromide and bromoacetic acid. Moreover, the production of pentabromomethyl acetate from citric acid is improbable on theoretical grounds. Grimaux also finds that bromoaciform may be produced by the action of bromine on acetone, the product thus obtained being identical with that which is prepared from citric acid. Hence Grimaux regards bromoaciform as pentabromacetone, $\text{OBr}^2\text{CO.CHBr}^2$.

BRONZE. See COPPER, ALLOYS OF.

BROOKITE, TiO_2 . This mineral, hitherto regarded as rhombic, appears from the recent investigations of A. Schrauf (*Jahrb. f. Min.* 1873, 754; 1877, 403), to be monoclinic with rhombic habit. This character explains the complete isomorphism of brookite with wolframite, and, as in the case of the latter, several types of brookite may be distinguished:—

$$\text{I. } a : b : c = 0.840269 : 1 : 1.0926735.$$

Angle of inclined axes = $90^\circ 35\frac{1}{2}'$.

To this type belong crystals from Tavistock and from Chamouni. Twins occur, having the axis of combination perpendicular to the orthopinacoid. The crystals exhibit numerous faces, the orthopinacoid predominating. Sp. gr. 4.16.

$$\text{II. } a : b : c = 0.84693 : 1 : 0.93795.$$

Angle of inclined axes = $90^\circ 39' 20''$.

Crystals from Ular; here also occur twins combined according to the preceding law. Sp. gr. 4.21.

$$\text{III. } a : b : c = 0.841419 : 1 : 0.943441.$$

Angle of inclined axes = $90^\circ 6' 30''$.

To this type belong most of the forms hitherto described as rhombic. Two twin-formations have been established; one (from Wales) with the axis of rotation perpendicular to $\infty P\infty$, the other (from Russia) with the axis of rotation perpendicular to $0P$. Sp. gr. 4.11.

Schrauf attributes these varieties to polymerism, and distinguishes sixteen forms of brookite, most of them exhibiting a great number of faces, and likewise refers arkanosite and eumannite to brookite.

The 'dispersion' in the plane of the optic axes exhibited by brookite is regarded by Schrauf as a further proof of the monoclinic character of this mineral.

G. vom Rath, on the other hand (*Jahrb. f. Min.* 1876, 201), infers from measurements of a remarkably fine crystal of brookite from the gold washings of Atliansk, near Miask in the Ural, that this mineral unquestionably belongs to the rhombic system. The crystal in question, 11 mm. long and 4 mm. thick, exhibits the combination ∞P . $P\infty$. P . $2P$. $\frac{1}{2}P$. $2P_2$. $5P_3$. $2P_4$. $\frac{3}{2}P_3$. $\frac{1}{2}P\infty$. $\frac{1}{2}P\infty$. $2P\infty$. $\infty P\infty$. $\infty P\infty$. $0P$.

BRUCINE, $\text{C}^{12}\text{H}^{16}\text{N}^2\text{O}^4$. This alkaloid crystallises in monoclinic prisms (E. Schmidt, *Deut. Chem. Ges. Ber.* x. 838).

Conversion into Strychnine.—The formula of strychnine, $\text{C}^{34}\text{H}^{52}\text{N}^2\text{O}^2$, may be derived from that of brucine by addition of 4 at. O, and elimination of $2\text{H}^2\text{O}$, and 2CO_2 , and this conversion is actually effected by the action of nitric acid. In fact, when brucine is gently heated with four or five times its weight of dilute nitric acid, the mixture becomes red, and carbonic anhydride is evolved. The red solution when concentrated on the water-bath, and agitated with ether, after addition of excess of potassium hydrate, gives a red ethereal solution, which, on evaporation, leaves a red colouring matter, a yellow resin, and a base. The latter, when purified by solution in acids and recrystallisation, gives the characteristic reactions of strychnine, and is identical therewith. This conversion of brucine into strychnine is of especial interest in its toxicological aspect, for it was found, on examining a mixture of lead nitrate and brucine for alkaloids by the Stass-Otto method (i. 125), that a base was isolated which gave the reactions of strychnine and not of brucine.

Conversely strychnine heated for several months to 100° in sealed tubes with a strong base, such as baryta, potash or soda, yields besides colouring matters and other products, a compound which resembles brucine in its behaviour with nitric acid, and, moreover, has a powerful reducing action, separating silver and platinum from their salts in the metallic state (Sonnenschein, *Deut. Chem. Ges. Ber.* viii. 212). See also Shenstone (*Pharm. J. Trans.* [3], viii. 652; *Chem. Soc. J.* 1877, ii. 499).

Detection of Brucine.—According to Pandis (*Chem. Centr.* 1872, 440), the delicate test for brucine is Dragendorff's modified nitric acid test. $\frac{1}{10}$ mgm. brucine, dissolved in sulphuric acid, gives, when a drop of nitric acid is allowed to come in contact with it in a watch-glass, at first a rose colour, then orange, and lastly yellow. The red-violet colour which is caused by addition of tin chloride or ammonium sulphide is not distinct with less than $\frac{1}{10}$ mgm. of the alkaloid.

Potassium iodide gives a kermes-coloured precipitate, even in a solution diluted 50,000 times. Potassium-bismuth iodide gives an orange-red precipitate in a 5,000 times diluted solution. The presence of strychnine does not affect the nitric acid test; neither does caffeine interfere with the detection of brucine.

* Struve (*Zeitschr. anal. Chem.* xii. 164) recommends the precipitation of brucine from mixed liquids by phosphomolybdic acid; even small traces of this precipitate will give with nitric acid the characteristic reaction of brucine.

According to J. H. Buckingham (*Pharm. J. Trans.* [3], iii. 884), a solution of ammonium sulphatomolybdate recently prepared by heating 8 grains of ammonium molybdate with two drachms of sulphuric acid, colours brucine brick-red.

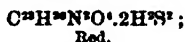
Flückiger (*Arch. Pharm.* [3], vi. 404) recommends *mercurous nitrate* as a delicate test for brucine. An aqueous solution of this salt (not containing free nitric acid) gives at first no coloration when added to the solution of a brucine salt. But if the mixture is gently heated on a water-bath, a fine carmine colour is produced, which is very durable. Strychnine does not give this reaction, so that one part of brucine can be detected by this means when mixed with ten to twenty parts of strychnine. The opium and cinchona alkaloids, also veratrine, caffeine, piperine, are not coloured by mercurous nitrate, but albumin and phenol act in the same way as brucine. The red colour produced by phenol, however, soon passes into brown. Brucine may be detected in presence of strychnine by evaporating the acetates to dryness, strychnine acetate being thereby decomposed, and yielding pure strychnine, while brucine acetate suffers little alteration. Cobalticyanide of potassium precipitates *dilute* solutions of the salts of strychnine, but not those of brucine.

Hydrosulphides of Brucine (E. Schmidt, *Deut. Chem.-Ges. Ber.* viii. 1267; x. 838).—Two of these compounds are formed by the action of hydrogen sulphide on an alcoholic solution of brucine, viz.:

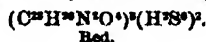
a. Yellow prismatic needles (m. p. about 125°) formed on passing a rapid stream of the gas into a strong solution of brucine in alcohol (1 : 10).

β. Ruby-red triclinic crystals (m. p. 155°) formed after a while in dilute solutions.

Schmidt at first assigned to these compounds the formulæ:



but by decomposing in hydrochloric acid solution with arsenious acid, and determining the quantities of arsenious sulphide and sulphur thereby precipitated (the process by which Hofmann analysed the corresponding strychnine-compounds *q. v.*) he finds that they contain not H^2S^2 but H^2S^4 , and are represented by the following formulæ:



BUCHONITE (F. Sandberger, *Münch. Akad. Ber.* 1872, 208; *Jahrb. f. Min.* 1873, 647).—A rock, belonging to the nephelenite group, occurring on the Calvarienberg, near Poppenhausen on the Rhön, on the Steinberg near Sinsheim in Baden, and in other localities, usually as a dark grey, fine-grained mass, in which are imbedded very thin laminae of a micaceous mineral, giving to the whole the appearance of porphyry. Examination with a lens shows also: white substances, some of which have a fatty lustre; black, highly lustrous hornblendes; and magnetic iron ore, often in well-developed octahedrons. In other very fine-grained portions, which have undergone alteration and have a blue-black colour, the same minerals are seen only after etching with acid, or in microscopic sections; then, however, augite and triclinic feldspars also come to light, but in much smaller crystals than the mica and hornblende. All the sections likewise exhibit hexagonal and needle-shaped crystals, mostly imbedded in the mica, which give the reactions of phosphoric acid, and doubtless consist of apatite.

In the variety from Poppenhausen, and less frequently in that from Sinsheim, there occur coarse-grained masses free from magnetic iron ore, but containing hornblendes in long prisms or radiating tufts of a raven-black colour; nepheline having a faint fatty lustre; orthoclase and mica; occasionally also apatite and plagioclase; chrysolite occurs sparingly in the Poppenhausen variety, more abundantly in that from Sinsheim. The mica forms black-brown hexagonal tables having almost a

vitreous lustre; it contains large quantities of ferrous and ferric oxides, but little alumina and magnesia, and much potash.

Buchonite is distinguished from nephelenite by the abundant and constant occurrence of hornblende, and of a mica which is not identical with biotite (true magnesia mica). Only the variety from Sinsheim has yet been analysed quantitatively, by C. Gmelin (*Leonhard's Beiträge*, i. 85), who found it to be composed as follows:

a. Gelatinising portion; b. Non-gelatinising portion; c. Total constituents, according to Roth's calculation:

	SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	
a. . .	35.91	18.45	28.98	3.13	4.02	2.41	5.34	1.23	= 99.47
b. . .	63.82	12.95	14.68	4.13	4.14	—	—	—	= 99.72
c. . .	51.42	15.39	21.04	3.68	4.09	1.07	2.37	0.55	= 99.61

Phosphoric acid, chlorine, and titanio acid were not determined.

The gelatinising is to the non-gelatinising portion in the proportion of about 3 : 4.

The analysis is sufficient to show the difference between buchonite and the nephelinite of the neighbouring Katzenbuckel, this difference being most conspicuous in the amounts of iron and alkali.

The medium-grained variety from the Calvarienberg at Poppenhausen has been analysed by E. v. Gerichten. Its specific gravity is 2.85. Its proximate constituents are nephelin, partly in course of transformation into natrolite; hornblende; a micaceous mineral; magnetic iron ore; triclinic and orthoclastic feldspar; apatite and augite. A large portion of it (40.73 p. c.) is decomposed by hydrochloric acid, with very distinct separation of gelatinous silica. This portion is therefore to the undecomposable portion in the ratio of 2 : 3, whereas in the Sinsheim rock this ratio is 3 : 4. The residue of the treatment with hydrochloric acid contains, after the silica has been removed by sodium carbonate, a very small quantity of augite, transparent colourless orthoclastic feldspar, and a small quantity of triclinic feldspar. Quantitative analysis gave: a. Portion soluble in hydrochloric acid (calculated to 100). b. Insoluble portion (calculated at 100)., c. Total constituents—

	SiO ₂ .	P ₂ O ₅ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	
a. . .	33.19	1.50	14.80	9.37	11.56	9.84	2.78	2.16	12.08	2.77	= 100.05
b. . .	54.64	—	14.46	10.68	2.34	7.15	0.44	5.25	5.04	—	= 100
c. . .	45.84	0.66	14.32	10.18	6.42	8.40	1.47	3.56	8.77	1.21	= 100.83

The small amount of magnesia and the large amount of iron in the insoluble residue show that the rock contains, not basaltic hornblende, but a hornblende rich in iron and poor in alkalis, like arfvedsonite, and the hornblende occurring in the zircon-syenite of Brevig. Orthoclase occurs abundantly in the residue, and is an essential constituent of the rock.

Notwithstanding the difference of mineralogical character, the total result of the analysis of buchonite is very much like that which Rosenbusch obtained for the porphyritic nephelenite of the Katzenbuckel (*Jahrbuch*, 1869, 47).

BUCHU. The leaves of several species of *Barosma* growing at the Cape, known as buchu leaves, contain an essential oil, which, by long exposure to the cold of winter, yields a well-crystallised camphor melting at 85° and beginning to sublime at 110°. It dissolves in carbon bisulphide, and crystallises therefrom in fine needles. The oil poured off from the camphor of *Barosma betulina* does not boil below 200°, and after rectification over soda answers to the formula C₁₆H₁₄O. The crude oil turns the plane of polarisation to the left (Flückiger, *Pharm. J. Trans.* [3], iv. 689).

A bustamite from Rézbanya in Hungary has been found by L. Sipőcz (*Min. Mitth.* 1873, 3) to contain:

SiO ₂	Al ₂ O ₃	FeO.	MnO.	MgO.	CaO.
47.44	1.17	6.54	23.13	1.16	21.02 = 100.46.

BUTANE, C₄H₁₀. On the nitro-derivatives of butane, see NITROPARAFFINS under PARAFFINS.

----- *Testing for Adulterations.*—Hoorn (*Zeitschr. anal. Chem.* 1872, 348) agitates the melted butter in a glass tube, narrowed and graduated in the

lower third of its length, with petroleum-ether (sp. gr. 0.69; m. p. 80°-110°). The impurities (water, &c.) then sink down to the lower part of the tube, where their amount can be read off, while the fatty matters are dissolved by the petroleum ether.

See also J. Campbell Brown (*Chem. News*, xxviii. 1 18, 31, 39, 43, 57, 69).

J. W. Gatehouse (*Chem. News*, xxxii. 297) describes a method of detecting the adulteration of butter with other fats, depending on the insolubility of potassium stearate in alkaline solutions. The butter is first boiled with water, and saponified at a high temperature with half its weight of solid potassium hydrate. If the butter is pure, the mass will have a faint yellow colour; if adulterated, it will mostly be black. The temperature must be kept above 200° C. for a few minutes, otherwise the stearate formed will not be insoluble in the alkaline liquid. The saponified mass is repeatedly boiled with water till the entire quantity of liquid exceeds 200 c.c. Part of this solution is poured into test-tubes, and its appearance observed. If it exhibits only a faint opalescence, the butter is pure; in the contrary case it is impure, the turbidity of the liquid increasing with the degree of impurity.

A method for the complete analysis of butter is given by A. H. Allen (*Chem. News*, xxxii. 77). The amount of water is determined by drying a weighed quantity of the butter at 110°-120°; that of fat, by exhausting the dried butter with petroleum. This leaves undissolved the casein and salts, together with any amylaceous substances, such as potatoes, flour, &c., that may have been added; these may then be further examined. A good unadulterated butter contains, on the average, 86 per cent. of fat. If the amount is less than 80 per cent. the butter may be regarded as adulterated.

Butter-fat differs from ordinary animal fats, such as beef or mutton suet, in containing the glycerides of volatile fatty acids (butyric, caproic, caprylic, &c.), in addition to those of the fixed fatty acids, stearic, palmitic, &c., which are the only acids present in suet and lard. In 117 samples of butter from various sources, analysed in the laboratory of the Board of Inland Revenue,* the proportion of fixed fatty acids was found to vary from 85.50 to 89.90 per cent., whereas beef suet gave 95.91 and fine lard 96.20 per cent.

The proportion of volatile acids in butter may be determined by saponifying the purified fat with potash, and decomposing the resulting soap with sulphuric acid, in presence of a quantity of water sufficient to dissolve the whole of the volatile fatty acids thereby set free. The total amount of free acid in the aqueous solution is estimated in a portion by standard soda, and calculated as H^2SO_4 ; a measured portion is then precipitated with barium chloride, and from this the total amount of sulphuric acid actually present in the liquid is calculated. Another portion is evaporated to dryness; the residue is heated in a covered platinum crucible till it ceases to fume; finally, with addition of ammonium carbonate; and the K^2SO_4 thus formed is calculated to H^2SO_4 , which gives the combined sulphuric acid. From these data the free sulphuric acid is obtained, and this deducted from the total amount of free acid gives the free acid other than sulphuric acid in the solution; this amount may be calculated to butyric acid (J. Muter, *Analyst*, 1876, p. 7; *Chem. Soc. J.* 1876, i. 233).

This method, however, like all others that have been devised for the direct estimation of the fatty acids of butter, takes up a considerable time, and is somewhat difficult of execution. An easier method is afforded by the determination of the specific gravity of the butter-fat, which for the most part increases very regularly as the proportion of fixed fatty acids in the butter diminishes. This may be seen from the following table (p. 358), extracted from the report above quoted on experiments made in the Inland Revenue laboratory.

The correspondence between the specific gravity of the fats and the percentage of fixed fatty acids, as shown by the table, is in fact close enough to admit of the determination of either number from the other within a few tenths of the whole. The slight variations observed in some cases are probably due to the fact that the several fixed fatty acids are not always present in different butters in exactly the same proportion.

The specific gravity of ordinary animal fats varies from 902.83 to 904.66, whereas that of butter-fat, as seen from the table, rarely falls below 910, the usual range being from 911 to 913 (water = 1000).

A method of facilitating the determination of the specific gravities of melted fats is described by C. Estcourt (*Chem. News*, xxxiv. 264).

* Report made to the Board of Inland Revenue by the Principal of the CHEMICAL LABORATORY, Somerset House, on experiments conducted by him for the analysis of butter, June 16, 1876.

Specific Gravity, Melting Point, and Percentage of Fixed Fatty Acids in Butter-fat.

Specific gravity at 100° F. (water = 1000)	Melting point	Percentage of fixed fatty acids	Specific gravity at 100° F. (water = 1000)	Melting point	Percentage of fixed fatty acids
913.89	87.5°	85.50	911.47	90°	87.66
912.79	88.5	86.00	911.60	92	87.74
912.89	88.5	86.45	911.41	92.5	87.79
912.69	89	86.60	911.29	90	87.90
910.91	91.5	86.79	910.78	90	88.00
912.39	89	86.87	911.79	90.5	88.05
912.23	88	86.87	911.34	93	88.12
912.51	89	86.90	910.80	92.5	88.17
912.08	90	86.92	910.63	93	88.32
912.01	90.5	86.96	910.93	92	88.35
912.39	92	87.01	910.94	92.5	88.40
912.44	89.6	87.14	911.06	93	88.42
912.28	87.5	87.20	910.85	92.5	88.46
912.28	87.8	87.30	910.91	90.5	88.46
911.90	89	87.30	910.85	92	88.62
911.46	90.5	87.35	911.79	90.5	88.65
911.60	92	87.40	910.66	92	88.74
912.08	89	87.42	910.19	92.5	88.75
912.03	90.5	87.42	910.14	92	88.90
911.40	89	87.50	909.87	92.5	89.15
911.50	93	87.61	909.39	95	89.80
911.74	91.6	87.60	909.37	94.5	89.90
911.79	90.6	87.65			

BUTYL ALCOHOLS AND ETHERS. 1. NORMAL PRIMARY COMPOUNDS. (Grabowsky a. Saytzeff, *Deut. Chem. Ges. Ber.* 1873, 1256; Grabowsky, *Lieb. Ann.* cxxxv. 348.)

potassiu

0° and

converted into butyl-sulphonic acid, the barium salt of which, $(C^4H^9SO^2)^2Ba + H^2O$, crystallises in transparent efflorescent plates.

Butyl Sulphide, $(C^4H^9)^2S$, prepared in like manner with potassium monosulphide, boils at 182°, and has a sp. gr. 0.8523 at 0°, 0.8386 at 16°, compared with water at 0°.

Butyl Oxysulphide, $(C^4H^9)^2SO$, is formed by treating the sulphide with nitric acid of sp. gr. 1.3. The action is energetic, even at ordinary temperatures, but to complete it, the mixture should be finally treated for a short time on the water-bath. The product, when cold, is diluted with water, and the oily layer removed by agitation with ether. The ethereal solution is next washed, first with water, then with a dilute solution of sodium carbonate, and again with water, after which the ether is removed by distillation. The oily residue, when allowed to cool, solidifies to a crystalline mass, which must be dried over sulphuric acid, and the liquid portion removed by draining. The *butyl oxysulphide* thus obtained crystallises in needles, which melt at 32°, and are decomposed by distillation. It is insoluble in water, but easily soluble in alcohol and ether.

Butylsulphone, $(C^4H^9)^2SO_2$, is prepared by slowly oxidising normal butyl sulphide with fuming nitric acid, and, when the reaction is complete, evaporating on the water-bath until the excess of nitric acid is completely removed. The residue is dissolved in ether, and washed, first with dilute soda-solution, then with water. On evaporating the ether, an oily liquid is left, which solidifies to a crystalline mass when dried over sulphuric acid. To purify this, it is pressed between paper, and recrystallised from alcohol, with addition of animal charcoal. It crystallises in plates, which melt at 43.5°, and are easily soluble in alcohol and ether. Both the oxide and the sulphone yield the normal mercaptan by reduction (Grabowsky).

2. ISOPRIMARY COMPOUNDS. **Isobutyl alcohol**, $CH(CH^3)^2.CH^2OH$, is converted by oxidation with chromic acid mixture into isobutyric acid and aldehyde, isobutylic isobutyrate, acetone, carbon dioxide, and water (Kraemer, *Deut. Chem. Ges. Ber.* vii. 252). Kraemer regards the acetone as a direct product of the oxidation of

the isobutyl alcohol; but according to E. Schmidt (*ibid.* 1361) it should rather be regarded as formed by further oxidation of the isobutyric acid formed in the first instance. It has in fact been shown by Popoff (*Zeitschr. f. Chem.* 1871, 4), that acetone is actually produced by oxidising isobutyric acid with aqueous chromic acid at 140°–150° in sealed tubes; and this statement is confirmed by Schmidt, who has, moreover, obtained considerable quantities of acetone by heating isobutyric acid with chromic acid mixture to 90°–100° in such a manner that the volatile products may distil off.

Isobutyl Bromide, $\text{CH}(\text{CH}_3)_2\text{CH}_2\text{Br}$. This ether heated in sealed tubes is gradually converted into tertiary butyl bromide, $\text{C}(\text{CH}_3)_3\text{Br}$, the result being brought about by a series of decompositions (into HBr and isobutylene) and recombinations (dissociation and association) going on simultaneously. On heating sealed tubes containing isobutyl bromide in the vapours of various benzoic ethers boiling between 213° and 250°, it is found (1) that the conversion is effected between 213° and 230°:

one-fifth of the total quantity employed. The rate of conversion depends upon the temperature. At 250° the limit is reached in an hour or two, or less; and since tertiary butyl bromide is gaseous at that temperature, the volume of the liquid gradually diminishes until (in most cases) the whole is vaporised, even when the free space above the liquid is but small.

On determining the vapour-density of the bromide by Dumas' method, at various stages of the process, it was found to begin to be abnormal at a temperature between 213° and 230°, coinciding therefore with the temperature at which the conversion into the tertiary bromide takes place.

By heating equal volumes of amyl bromide in tubes of the same diameter, but of different lengths, it was found that the rate of conversion depends upon the amount of free space above the liquid, whence it appears that the conversion takes place chiefly in the vapour (Elketoff, *Deut. Chem. Ges. Ber.* viii. 1244).

Isobutyl Carbonates and Thiocarbonates (Mylius, *Deut. Chem. Ges. Ber.* v. 972). **Isobutyl Chlorocarbonate**, $\text{C}^i\text{H}^i\text{O}\left\{\begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix}\right\}\text{CO}$, is formed by saturating isobutyl-alcohol with carbon oxychloride. It is a liquid, resembling the ethyl-compound, and distilling with much decomposition at 130°–140°. With ammonia it yields **isobutyl-urethane**, $\text{C}^i\text{H}^i\text{O}\left\{\begin{smallmatrix} \text{O} \\ \text{NH}_2 \end{smallmatrix}\right\}\text{CO}$, a solid melting at 55° and boiling at 206°–207°, not at 220°, as stated by Humann, who obtained it by the action of cyanogen chloride on isobutyl alcohol. **Isobutyl-phenylurethane**, $\text{C}^i\text{H}^i\text{O}\left\{\begin{smallmatrix} \text{O} \\ \text{C}^i\text{H}^i\text{NH} \end{smallmatrix}\right\}\text{CO}$, obtained by mixing ethereal solutions of the chlorocarbonate and aniline, crystallises in soft white needles, melting at 80° and boiling at 216°, a small portion being resolved into the alcohol and phenyl cyanate. It is readily soluble in ether and alcohol, but sparingly in water. The corresponding tolyl derivative, obtained from liquid toluidine boiling at 198°, is an oily liquid, boiling with partial decomposition at 275°–280°.

Potassium Isobutylxanthate, $\text{C}^i\text{H}^i\text{O}\left\{\begin{smallmatrix} \text{O} \\ \text{KS} \end{smallmatrix}\right\}\text{CS}$, formed on adding carbon disulphide to a solution of potash in isobutyl alcohol, crystallises from alcohol in yellowish-white needles, and is resolved by destructive distillation into carbonic oxide, isobutyl sulphide. The **sodium salt** is a similar body, which is very freely soluble in water, alcohol, and a mixture of ether and alcohol.

Ethylis Isobutylxanthate, $\text{C}^i\text{H}^i\text{O}\left\{\begin{smallmatrix} \text{O} \\ \text{C}^i\text{H}_3\text{S} \end{smallmatrix}\right\}\text{CS}$, is obtained by heating the potassium salt with ethyl iodide to 100°. It is a yellow liquid boiling at 227°–228°, having a disagreeable smell and a taste like that of aniseed. By the action of isobutyl iodide on the potassium salt, **isobutylis isobutylxanthate**, $\text{C}^i\text{H}^i\text{O}\left\{\begin{smallmatrix} \text{O} \\ \text{C}^i\text{H}_3\text{S} \end{smallmatrix}\right\}\text{CS}$, is produced, a liquid boiling at 247°–250°, and having a sp. gr. of 1.009 at 12°. The corresponding **amyl-ether** is formed only at 140°. It boils at 265°–270°, with decomposition, being partly resolved into carbonic oxide, and the sulphides of amyl and isobutyl.

Isobutyl Dioxythiocarbonate, $(\text{C}^i\text{H}^i\text{O}.\text{CS})_2\text{S}$, is obtained as a yellow heavy oil when chlorine is passed into an aqueous solution of potassium isobutylxanthate. By the action of sodium, it is converted into sodium isobutylxanthate; and when ammonia is passed into its ethereal solution, it yields the **semi-sulphurated urethane**, $\text{C}^i\text{H}^i\text{O}\left\{\begin{smallmatrix} \text{O} \\ \text{NH}_2 \end{smallmatrix}\right\}\text{CS}$, crystallising from alcohol or ether in large, yellowish-white rhombic

plates, melting at 36° . On distillation, the greater portion is resolved into cyanic acid and isobutyl mercaptan.

When ethereal solutions of equivalent quantities of aniline and isobutyl dioxithiocarbonate are mixed, the liquid becomes warm, sulphur separates out, and on evaporation a residue consisting of a mixture of isobutyl phenylthiocarbamate and diphenylthiocarbamide is left behind. In this reaction first the semisulphuretted urethane,

$\begin{matrix} \text{O}^{\text{H}^{\text{O}}} \\ \text{C}^{\text{H}^{\text{N}}} \end{matrix} \text{OS}$, is formed, together with aniline isobutyl-xanthate; the latter compound easily splits up into aniline, carbon sulphide, and isobutyl alcohol, and the aniline thus set free transforms the urethane into the thiocarbamide.

To prevent the action of aniline on the urethane, the liquid has to be kept cold, and, as soon as the separation of sulphur ceases, a quantity of hydrochloric acid must be added, sufficient to neutralise half the aniline employed. The phenylurethane thus produced melts at 75° , and has a bitter taste and agreeable odour. It cannot be distilled without decomposition, but evaporates completely on a water-bath.

Isobutyl Oxalate, $(\text{C}^{\text{H}^{\text{O}}})^2\text{C}^{\text{O}}^4$, is easily obtained by distilling a mixture of oxalic acid partly deprived of water, and anhydrous isobutyl alcohol. It is a very clear, colourless liquid, insoluble in water, but miscible in all proportions with alcohol and ether. Its sp. gr. is 1.002 at 14° . Boiling point 224° - 226° . A boiling solution of potash decomposes it rapidly, furnishing an oxalate, but with a limited quantity of potash it gives *potassium-isobutyl oxalate*, $(\text{C}^{\text{H}^{\text{O}}})\text{KC}^{\text{O}}^4$. Similarly excess of ammonia gives rise to oxamide; but an alcoholic solution of ammonia, added gradually, converts it into *isobutylic oxamate*, $\text{CO}(\text{NH}^2)(\text{OC}^{\text{H}^{\text{O}}})$, which crystallises in fine prisms (Cahours, *Compt. rend.* lxxviii. 1403).

Isobutyl Orthosilicate, $(\text{C}^{\text{H}^{\text{O}}})^4\text{SiO}^4$, is prepared by adding gradually 4 mols. of isobutyl alcohol to 1 mol. of silicon tetrachloride contained in a retort, and submitting the product to distillation. The pure ether boils between 256° and 260° , and its sp. gr. is 0.953 at 15° . It is decomposed very slowly by water or by contact with moist air.

Silicon chloride reacts upon isobutyl orthosilicate, probably forming chlorhydrins, which have not yet been investigated (Cahours, *loc. cit.*)

Isobutyl Sulphide, $(\text{C}^{\text{H}^{\text{O}}})^2\text{S}$, is a light liquid smelling like other alcoholic sulphides, and boiling at 172° - 173° . Nitric acid converts it into isobutyl dioxysulphide, $(\text{C}^{\text{H}^{\text{O}}})^2\text{SO}^2$, which is almost insoluble in water, freely soluble in alcohol and ether, and crystallises in needles melting at 41° and resolidifying at 30° (Grabowsky a. Seytzeff, *Liebig's Annalen*, clxxi. 251).

Isobutylsulphonic acid, $\text{CH}(\text{C}^{\text{H}^{\text{O}}})^2\text{CH}^2\text{SO}^3\text{H}$, is obtained by oxidising isobutyl mercaptan with nitric acid of sp. gr. 1.30; at the same time an oily compound is formed, which, however, is not the chief product of the reaction, the quantity of it being smaller as the mercaptan is purer, that is to say, in proportion as it contains a smaller quantity of isobutyl sulphide.

By decomposing the lead salt of isobutylsulphonic acid with hydrogen sulphide, and evaporating the solution on a water-bath, isobutylsulphonic acid is obtained as a syrupy liquid, which, in a vacuum over sulphuric acid, changes into a crystalline magma. The salts of this acid are all extremely soluble in water. *Silver isobutylsulphonate*, $\text{C}^{\text{H}^{\text{O}}}\text{SO}^3\text{Ag}$, forms crystalline scales which are not acted upon by light. *Barium isobutylsulphonate*, $(\text{C}^{\text{H}^{\text{O}}}\text{SO}^3)^2\text{Ba}$, is precipitated from a concentrated aqueous solution by alcohol in thin white needles. The *copper salt* forms soft sea-green scales.

Metallic Isobutyliides (Cahours, *Compt. rend.* lxxvii. 1403). The *aluminium compound*, $\text{Al}(\text{C}^{\text{H}^{\text{O}}})^3$, is formed by the action of aluminium on mercuric isobutyliide (*infra*). It is a colourless liquid which fumes in the air.

Mercuric Isobutyliide, $\text{Hg}(\text{C}^{\text{H}^{\text{O}}})^2$, is obtained by treating a mixture of isobutyl iodide and ethyl acetate with a 2 per cent. sodium-amalgam. The action of water on the resulting pasty mass causes the separation of a heavy liquid which yields mercuric isobutyliide on rectification. The product is a colourless refractive liquid which distils between 205° and 207° . Its sp. gr. is 1.835 at 15° . It is soluble in water, alcohol, and ether. Acted upon by bromine or iodine, it yields mercuric bromo- or iodo-butyliide, and these compounds heated with oxide of silver and water give the corresponding basic hydrate, $\text{Hg}(\text{C}^{\text{H}^{\text{O}}})\text{HO}$, which crystallises by evaporation over sulphuric acid.

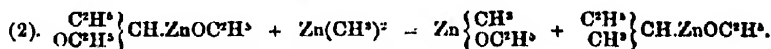
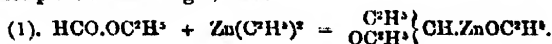
Stannic Isobutyliides.—Isobutyl iodide, heated for a few hours to 100° with an alloy of tin and sodium, forms stannic tri-isobutyl iodide, $\text{Sn}\left\{(\text{C}^{\text{H}^{\text{O}}})^2\right\}_3$, as a yellow oily liquid, which boils between 292° and 296° , and has a sp. gr. = 1.64 at 15° .

Distilled from moist potash it gives iodide of potassium and a distillate consisting of a colourless, viscid liquid which gradually concretes into a solid but not distinctly crystalline mass. This oxide has a strong alkaline reaction, and neutralises acids, forming salts which generally crystallise readily. In the reaction between the butyl iodide and the sodium-zinc alloy, a very small quantity of a crystalline body is produced, which is probably $\text{Sn}(\text{C}^4\text{H}^9)_2\text{I}^2$.

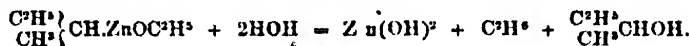
Zinc Isobutylide, obtained by the action of zinc on the mercuric compound, is a colourless, fuming, inflammable liquid which boils at 185° – 188° . Water decomposes it violently. The trichlorides of phosphorus and arsenic react with it energetically, producing phosphines and arsines not yet examined.

Powdered arsenic acts upon isobutyl iodide at 175° – 180° , giving rise to a reddish crystalline compound of arsenic iodide and tributyl-arsine.

SECONDARY BUTYL COMPOUNDS. *Secondary Butyl Alcohol*, or *Ethyl-methyl Carbinol*, $\begin{smallmatrix} \text{CH}^3 \\ | \\ \text{C}^2\text{H}^5 \end{smallmatrix} \text{CHOH}$, is produced by the action of ethyl formate on a mixture of zinc-ethyl and zinc-methyl,—or better (as in the preparation of diethyl-carbinol, p. 78), by gently heating a mixture of 1 mol. ethyl formate, 2 mols. ethyl iodide, and 2 mols. methyl iodide, with granulated zinc and a zinc-sodium alloy, whereby the zinc-compounds of methyl and ethyl are produced in the nascent state, and then acted on by the formic ether. The reaction, which is energetic at first, is known to be terminated when the contents of the flask solidify to a brown crystalline mass. It takes place in two stages, viz.:



The product, added to a mixture of ice and water, is decomposed in the manner shown by the equation:



To purify the ethyl-methyl carbinol thus obtained, it is distilled with hydrochloric acid; the distillate, as in the preparation of diethyl carbinol, is collected in two portions, and the butyl alcohol is separated from the aqueous liquor by potassium carbonate, and converted into the corresponding iodide by gaseous hydriodic acid.

This iodide, $\begin{smallmatrix} \text{C}^2\text{H}^5 \\ | \\ \text{CH}^3 \end{smallmatrix} \text{CHI}$, boils, after fractionation, between 119° and 120° , and the methyl-ethyl carbinol prepared from it by digestion with lead hydrate and water, distils at 98° – 100° . The alcohol gradually oxidised with chromic acid mixture yields methyl-ethyl ketone, $\text{CH}^3.\text{CO}.\text{C}^2\text{H}^5$, boiling at 80° , together with acetic acid (Kannonikoff & Saytzeff, *Liebig's Annalen*, clxv. 374).

Secondary Butyl Ether, or **Ethyl-methyl Carbinyl Oxide**, $\begin{smallmatrix} \text{C}^2\text{H}^5 \\ | \\ \text{CH}^3 \end{smallmatrix} \text{CH}-\text{O}-\text{CH} \begin{smallmatrix} \text{C}^2\text{H}^5 \\ | \\ \text{CH}^3 \end{smallmatrix}$, prepared by the action of zinc-ethyl on ethidene oxy-chloride, $\text{CH}^3-\text{CHCl}-\text{O}-\text{CHCl}-\text{CH}^3$, in etheral solution, and purified by fractional distillation, boils between 120° and 122° , and is converted by heating with fuming hydriodic acid into the corresponding iodide, $(\text{C}^2\text{H}^5)(\text{CH}^3)\text{CHI}$, which boils at 117° – 118° (Kessel, *Deut. Chem. Ges. Ber.* vii. 201).

Secondary Butyl Mercaptan, $\begin{smallmatrix} \text{C}^2\text{H}^5 \\ | \\ \text{CH}^3 \end{smallmatrix} \text{CH}.\text{SH}$, prepared by digesting the corresponding iodide (from erythrite) with an alcoholic solution of potassium sulphhydrate, is a mobile liquid smelling like asafetida, boiling at 84° – 85° , and having at 17° the sp. gr. 0.8299. On mixing its alcoholic solution with mercuric chloride, a white amorphous precipitate is formed, which crystallises from boiling alcohol in greasy scales melting at 189° , and consisting of $(\text{C}^4\text{H}^9\text{S})_2\text{Hg}$. The *silver mercaptide*, $\text{C}^4\text{H}^9\text{S}.\text{Ag}$, is a similar body, forming very small and slender needles. The *copper compound* is a yellow precipitate, which is easily decomposed; the *lead salt* forms a yellow unctuous mass.

Secondary Butylsulphide, $(\text{C}^4\text{H}^9)_2\text{S}$, is a mobile liquid boiling at 165° and having an alliaceous odour; its sp. gr. is 0.8317 at 23° . By the action of methyl iodide, it is not converted into dibutylmethylsulphine iodide, but suffers complete decomposition, yielding a crystalline solid, probably trimethylsulphine iodide, besides other products (S. Reymann, *Deut. Chem. Ges. Ber.* vii. 1287).

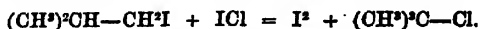
3. TERTIARY BUTYL-COMPOUNDS. Several ways of producing these com-

BUTYL ALCOHOLS AND ETHERS.

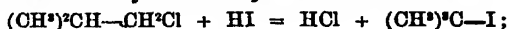
from isobutyl compounds have been mentioned in the 2nd Supplement (219-221): thus isobutylene (from isobutyl iodide) unites with hydriodic, hydro-sulphuric, or sulphuric acid, producing trimethyl-carbinyl iodide or chloride, or trimethyl-carbinyl-sulphuric acid: e.g.



and isobutyl iodide is converted by iodine monochloride into trimethyl-carbinyl chloride:



In like manner, isobutyl chloride may be converted into trimethyl-carbinyl iodide, or chloride by the action of hydriodic or hydrochloric acid: thus—



and this reaction may account for the supposed production of tertiary butyl alcohol in alcoholic fermentation which has been observed in some instances. Thus Butlerow (*Liebig's Annalen*, cxliv. 34), in preparing isobutyl chloride from commercial butyl alcohol, found that it was mixed with tertiary butyl chloride; and a similar observation has lately been made by Freund (*J. pr. Chem.* [2], xii. 25), with regard to a fusel-oil obtained from a potato-spirit factory. On subjecting this fusel-oil to fractional distillation, a considerable quantity passed over between 107° and 110°, and on converting this portion into chloride by heating with hydrochloric acid in a sealed tube, much isobutyl chloride was obtained boiling between 66.5° and 66°, together with a chloride boiling between 50° and 53°; and this latter chloride, when heated for ten hours in a water-bath with 4 parts of water in sealed tubes, gave an alcohol which, after desiccation, boiled at 80°-85°, was solid at ordinary temperatures, and therefore consisted of trimethyl-carbinol. The same result was, however, obtained when perfectly pure isobutyl alcohol was heated with hydrochloric acid, and the resulting chloride was heated with water, trimethyl-carbinol being obtained, and in quantity continually increasing with the proportion of hydrochloric acid employed. Hence it is inferred that the trimethyl-carbinyl chloride obtained by heating the fusel-oil above mentioned with hydrochloric acid was due, not to tertiary butyl alcohol originally contained therein, but to the action of the hydrochloric acid on the isobutyl chloride formed in the first instance.

Action of Chlorine on Trimethyl Carbinol.—When chlorine is passed to saturation through trimethyl-carbinol, the reaction being assisted towards the end by a gentle heat, the liquid separates into two layers, one of which consists of aqueous hydrochloric acid, the other of a mixture of high-boiling chlorinated compounds, the chief of which has the composition of pentachlorobutylene, C_4HCl_5 . This compound is a liquid of camphor-like odour, boiling at 185°-188° under a pressure of 460 mm., heavier than water, and not appreciably affected thereby. It may be regarded as resulting, together with water, from the splitting up of a chlorinated derivative of the alcohol not yet isolated (F. Loidl, *Deut. Chem. Ges. Ber.* viii. 1017).

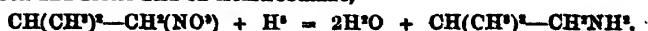
Tertiary Butyl Cyanide. *Trimethyl-carbinyl Cyanide*, or *Trimethyl-acetonitril*, $(\text{CH}_3)_3\text{C}-\text{CN}$ (Butlerow, *Liebig's Annalen*, clxx. 151).—This compound is formed by the action of tertiary butyl iodide at low temperatures on potassio-mercuric cyanide. 100 parts of tertiary butyl iodide are mixed in a vessel immersed in water at a temperature not exceeding 5°, with 110 parts of pulverised and dried potassio-mercuric iodide and 75 parts of talc-powder (to thicken the mass). The reaction begins spontaneously, and goes on, if the temperature be kept low, for two or three days, whereas if the cooling be neglected it becomes rapid and even violent, and yields a much smaller product. On adding water after the reaction is finished, and distilling from a paraffin-bath, an oil passes over, and potassio-mercuric iodide remains in the retort, together with resinous products. The oil, dried over calcium chloride and subjected to repeated fractional distillation, is resolved into a portion boiling at 105°-106°, another boiling at about 165°, and intermediate fractions consisting of mixtures of the two.

The fraction boiling at 105°-106° is tertiary butyl cyanide. It solidifies on cooling to a crystalline mass, which melts at 15°-16°, has a peculiar pungent odour, burns with a bright but very smoky flame, and when heated to 100° with strong hydrochloric acid, is completely converted into trimethyl-acetic acid, $\text{C}(\text{CH}_3)_3\text{COOH}$. With potash it yields scarcely any butylamine.

The portion boiling at 165° is probably the formamide of tertiary butyl, for when heated with alcoholic potash solution it yields a large quantity of butylamine (containing tertiary butyl) but no trimethylacetic acid; but when heated with hydrochloric acid it yields trimethylacetic acid, sal-ammoniac, and hydrochloride of butylamine. Heated with phosphoric anhydride it appears to be converted, at least in

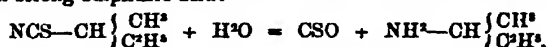
part, into tertiary butyl cyanide. It behaves therefore like the formamides of the aromatic series described by Hofmann.

BUTYLAMINES. *Isobutylamine*, $\text{NH}^2\text{—CH}^2\text{CH}(\text{CH}^3)^2$, is formed by the action of iron and acetic acid on isonitrobutane,



On warming the nitro-compound with excess of finely divided iron and dilute acetic acid on the water-bath, till its peculiar smell is no longer perceptible, then distilling with potash, and receiving the vapour in dilute hydrochloric acid, there remains on evaporation a white hygroscopic hydrochloride, easily and completely soluble in hydrochloric acid, and giving with platinic chloride a platinum salt, $2(\text{C}^4\text{H}^{11}\text{N.HCl}).\text{PtCl}_4$, which separates from the concentrated solution in golden-yellow laminae having a satiny lustre (Demole, *Liebig's Annalen*, clxxv. 142); compare v. 737.

Secondary Butylamine, $\text{NH}^2\text{—CH}\left\{\begin{smallmatrix} \text{CH}^3 \\ \text{C}^2\text{H}^5 \end{smallmatrix}\right.$, is produced by heating secondary butyl thio-carbimide, $\text{NCS—CH}(\text{CH}^3)(\text{C}^2\text{H}^5)$, either synthetically prepared or obtained by rectification from the volatile oil of scurvy-grass, *Cochlearia officinalis* (see THIOCARBIMIDES), with strong sulphuric acid:



Carbon oxysulphide is then evolved, and an amine sulphate is obtained, from which the base may be separated by distillation with caustic alkali. By treatment with solid potassium hydrate, and finally by prolonged contact with recently pressed sodium-wire, it is obtained as a colourless very mobile liquid boiling at 63° (normal primary butylamine boils at 75.6° , isobutylamine at $62^\circ\text{--}65^\circ$).

Secondary butylamine precipitates the salts of lead, magnesium, copper, silver, and aluminium, like the normal amine (2nd Suppl. 222); but while the latter redissolves the silver- and copper-precipitates, the secondary amine dissolves only the hydroxides of silver and aluminium, but neither that of copper nor that of zinc, which latter is soluble in isobutylamine (v. 737).

A further distinction between isobutylamine and secondary butylamine is afforded by their behaviour with ethyl oxalate, the former yielding an immediate precipitate of isobutyloxamide, even in the cold, whereas the latter is not acted on by oxalic ether even at 100° .

Reimer, by heating isobutylamine with isobutyl iodide, obtained the corresponding di- and tri-butylamines, but not the iodide of tetrabutylammonium (2nd Suppl. 222); and Reymann finds that secondary butylamine treated in like manner with secondary butyl iodide yields a considerable quantity of butylene, together with a mixture of di- and tri-butylamine, in which the proportion of the latter seems to be very small. The facility with which the more highly substituted amines are formed from alcohols containing the same number of carbon atoms appears therefore to diminish from the normal primary to the tertiary alcohol. From normal butyl alcohol (as from methyl and ethyl alcohols) the whole series of butylamines may be obtained up to tetrabutylammonium; isobutyl alcohol yields the three amines, but not the quaternary bases; secondary butylamine appears to yield tributylamine only with great difficulty; and from tertiary butyl alcohol even the corresponding monobutylamine has hitherto been obtained only by circuitous processes.

BUTYLENE, C^4H^6 . Three modifications of this hydrocarbon are known, viz.:

Normal Butylene, $\text{CH}^2\text{—CH}^2\text{—CH}=\text{CH}^2$.

Pseudobutylene, $\text{CH}^2\text{—CH}=\text{CH—CH}^2$.

Isobutylene, $(\text{CH}^3)^2\text{C}=\text{CH}^2$.

The first may be formed by abstraction of HI from normal primary butyl iodide, $\text{CH}^2\text{—CH}^2\text{—CH}^2\text{—CH}^2\text{I}$; or from secondary butyl iodide (methyl-ethyl-carbinyl iodide), $\text{CH}^2\text{—CH}^2\text{—CHI—CH}^2$; the second, in like manner, from secondary butyl iodide; and the third from isobutyl iodide, $\text{CH}(\text{CH}^3)^2\text{—CH}^2\text{I}$, or from tertiary butyl iodide, $(\text{CH}^3)_3\text{CI}$ (2nd Suppl. 223).

1. Normal butylene, obtained from normal butyl iodide, has lately been examined by Grabowsky a. Saytzeff (*Liebig's Annalen*, clxxix. 326). The iodide, prepared by passing hydriodic acid gas into normal butyl alcohol (obtained by reduction of butyryl chloride) (2nd Suppl. 215), was decomposed by alcoholic potash; the butylene thereby produced was passed directly into bromine; and the resulting butylene bromide, after being washed and dried, was distilled, the greater part passing over between 160° and 170° ; and from this, by further fractionation, pure butylene bromide was obtained boiling constantly at $164^\circ\text{--}165^\circ$. This bromide has a characteristic odour, and is partly decomposed by distillation, giving off vapours of hydrobromic acid. Its sp. gr. at 0° is 1.8503, and its coefficient of expansion for one degree between

0° and 20° is 0.00082. These properties show that it is identical with the bromide of ethyl-vinyl prepared by Wurtz (1st Suppl. 377), and therefore that the butylene prepared from normal butyl alcohol has the constitution represented by the first of the three formulæ above given.

2. Pseudobutylene is formed by the action of alcoholic potash, silver oxide and water, or silver acetate, on secondary butyl iodide; by heating secondary butyl alcohol to 260°; and by the decomposition of amyl alcohol at a red heat (v. 737); also, together with isobutylene, by distilling isobutyl alcohol with zinc chloride (Névolé, *Bull. Soc. Chim.*) It boils at +8°; solidifies to a crystalline mass at very low temperatures; unites with hydriodic acid to form secondary butyl iodide. Its bromide, $\text{CH}^3\text{—CHBr—CHBr—CH}^3$, boils at 150°.

Methyl-allyl, obtained by the action of sodium on a mixture of the iodides of allyl and methyl (1st Suppl. 376) is most probably identical with pseudobutylene. It yields a bromide boiling at 156°–159°, unites with hydriodic acid to form secondary butyl iodide, and in fact differs from pseudobutylene only in its boiling point, which is said to be between –4° and –8°; but the determination of boiling points at these low temperatures is somewhat uncertain.

3. Isobutylene boils at –6°; unites with hydriodic acid to form tertiary butyl iodide, and with strong hydrochloric acid at 100°, to form tertiary butyl chloride. It is absorbed by strong sulphuric acid, forming a sulpho-acid which, when diluted with water and distilled, yields tertiary butyl alcohol (1st Suppl. 376; 2nd Suppl. 219). It is also converted into tertiary butyl alcohol by direct combination with water, when kept for some time in sealed tubes, together with water mixed with $\frac{1}{10}$ of its volume of nitric acid and an equal volume of alcohol (Fittig's *Grundriss d. org. Chemie* 10te Auflage, 145). According to Butlerow (*Deut. Chem. Ges. Ber.* viii. 1017), liquid isobutylene is converted by dilute sulphuric acid at ordinary temperatures into tertiary butyl alcohol, but at high temperatures in sealed tubes into di-isobutylene.

Isobutylene bromide boils at 147°–148° (Névolé, *Compt. rend.* lxxiii. 65). Isobutylene chlorhydrin, $(\text{CH}^3)_2\text{—CCl—CH}^2\text{—OH}$, from isobutylene and hypochlorous acid, is a liquid boiling at 128°–130°, and converted by oxidation into chlorisobutyric acid (L. Henry, *Bull. Soc. Chim.* [2], xvi. 23).

BUTYLENE ALCOHOLS or BUTYL GLYCOLS, $\text{C}^4\text{H}^{10}\text{O}^2 = \text{C}^4\text{H}^8(\text{OH})^2$. Of these compounds, four isomeric modifications are known, viz. :—

(1). $\text{CH}^3\text{—CH}(\text{OH})\text{—CH}^2\text{—CH}^2\text{OH}$. Formed by the action of sodium-amalgam on acetaldehyde, or better on aldol (p. 54), produced therefrom. It is a colourless viscid liquid easily soluble in water; boils at 203.5°–204°; converted by oxidation first into crotonic aldehyde, then into acetic and oxalic acids (2nd Suppl. 225).

(2). $\text{CH}^3\text{—CH}^2\text{—CHOH—CH}^2\text{OH}$. From normal butylene bromide by saponification with caustic potash or baryta. The potash, previously fused and pulverised, is added to the bromide by small portions, the mixture being carefully stirred, and the glycol is then distilled off. In saponifying with baryta, the butylene bromide is diluted with water; the baryta is added in quantity sufficient to produce a strong alkaline reaction; and the liquid is heated on the water-bath for 24 hours, and, if necessary, mixed with fresh portions of baryta, and again heated.

The butyl glycol thus obtained is a viscid liquid, easily soluble in water and alcohol, boiling at 191°–192°, and having a density of 1.0189 at 0°. By rapid oxidation with nitric acid of ordinary strength, it is almost wholly converted into oxalic acid; but, by regulated oxidation, 1 pt. of the glycol being mixed in a test-tube immersed in water with 2 pts. nitric acid of sp. gr. 1.31, and 4 pts. water, it is converted into glycollic and glyoxylic acids (Grabowsky a. Saytzeff, *Liebig's Annalen*, clxxix. 325).

(3). $\text{CH}^3\text{—CHOH—CHOH—CH}^3$. Obtained by Wurtz from pseudobutylene bromide (v. 739). Colourless, inodorous, viscid liquid, boiling at 183°–184°, and having a density of 1.048 at 0°. Mixes in all proportions with water and with alcohol; oxidised by nitric acid to oxalic acid.

(4). $\begin{matrix} \text{H}^2\text{C} \\ \text{H}^2\text{C} \end{matrix} > \text{COH—CH}^2\text{OH}$. From isobutylene bromide (b. p. 147°–148°) by heating for several days with potassium carbonate. It boils at 176°–178°; has a density of 1.0129 at 0°, and 1.003 at 20°; dissolves easily in water and in alcohol. It is oxidised by potassium permanganate to carbonic and acetic acids; by chromic acid, apparently to acetic acid. Heated with nitric acid of sp. gr. 1.33, it forms an ethereal layer, from which, by distillation, a liquid may be obtained passing over between 136° and 138°, and having the composition $\text{C}^4\text{H}^{10}\text{O}^2$. This liquid is attacked by hydrobromic acid and by phosphorus pentachloride, not by sodium or by baryta (Névolé, *Compt. rend.* lxxiii. 65, 146).

BUTYL PHOSPHINES. See PHOSPHINES (2nd Suppl. p. 956).

BUTYRIC ACIDS, $C^4H^8O^2$. Normal butyric acid and ethyl butyrate were observed by Schützenberger (*Compt. rend.* lxxx. 328) to be formed by the fermentation of a sugar-juice in which twigs of *Elodea canadensis* were immersed. Carbon dioxide and hydrogen were evolved at the same time, and alcohol was found in the fermented juice.

Butyric acid, heated with nitric acid of sp. gr. 1.4 in a retort with reversed condenser, or in sealed tubes, is converted into succinic acid, as formerly observed by Des-saignes (i. 692):

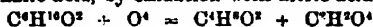


As, however, succinic acid readily undergoes further oxidation under the influence of nitric acid, it is best to heat the butyric acid with a quantity of nitric acid less than sufficient for its complete conversion into succinic acid, then separate the unaltered butyric acid, treat it with a fresh portion of nitric acid, and so on till the whole is oxidised. By thus treating butyric acid five times in succession with small quantities of nitric acid, the yield of succinic acid is five times as great as that obtained by at once heating the same quantity of butyric acid with a large quantity of nitric acid (Erlenmeyer, Sigel & Belli, *Liebig's Annalen*, clxxx. 207).

Isobutyric Acid. *Formation from Normal Butyric Acid.*—A solution of calcium butyrate saturated in the cold, which had been kept for ten years in a sealed tube, and heated some thirty or forty times—for the purpose of demonstrating the separation of the salt from its solution under the influence of heat—was ultimately found not to exhibit this separation any longer in consequence of the conversion of about one-tenth of the normal butyrate into isobutyrate. The same result was not produced by boiling a solution of normal calcium butyrate for eight hours (Erlenmeyer, *Liebig's Annalen*, clxxxi. 126).

From Pyrotartronic acid.—a. Together with acetic acid, by the action of melting potash: $CH(CH^3)^2-CH=CH-CO^2H + 2H^2O = CH(CH^3)^2.CO^2H + CH^3-CO^2H + H^2$.

b. Together with oxalic acid, by oxidation with nitric acid:



(W. C. Williams, *Deut. Chem. Ges. Ber.* vi. 1094).

Bromobutyric Acids. Two isomeric bromobutyric acids, viz.



convertible into the corresponding oxybutyric acids, are formed by the action of bromine at the heat of the water-bath, on normal butyric acid (Pupoff, *Deut. Chem. Ges. Ber.* vi. 1094).

Bromoisobutyric acid, $(CH^3)^2CBr.CO^2H$ (Hell & Waldauer, *ibid.* x. 448; compare 1st Suppl. 379). This acid, obtained by heating molecular proportions of bromine and isobutyric acid to 140° in sealed tubes, is a white, nearly inodorous, crystalline mass, melting at 48° . By slow evaporation of its ethereal solution, it may be obtained in large tabular crystals. It boils with slight decomposition at $198^\circ-200^\circ$. Sp. gr. at $60^\circ = 1.5226$; at $100^\circ = 1.500$, water at the same temperatures being 1. It dissolves in alcohol, ether, carbon bisulphide, chloroform, benzene, &c. When boiled with water, it is slowly but completely resolved into hydrobromic acid and oxyisobutyric acid. It is completely decomposed by aqueous silver nitrate, slowly in the cold, more rapidly when heated.

The *ethyllic ether* of monobromoisobutyric acid, obtained by passing hydrogen chloride into an alcoholic solution of the acid, boils at 180° (corr.)

Monobromoisobutyric acid in alcoholic solution is decomposed by alcoholic potash, yielding potassium bromide and the potassium salt of the following acid.

Ethoxymoisobutyric acid, $(CH^3)^2C(OC^2H^5).COOH$, obtained by decomposing monobromoisobutyric acid in alcoholic solution with alcoholic potash, converting the resulting potassium salt into a barium salt, and decomposing the latter with sulphuric acid, is a colourless liquid of penetrating ethereal odour and pungent burning taste, soluble in alcohol and ether, sparingly in water. It boils at 180° under a pressure of 741 mm. Sp. gr. = 1.0211 at 0° ; 1.0101 at 16° , water at the same temperatures being 1. It forms easily soluble and crystallisable salts.

The *silver salt*, $C^4H^7O^3Ag$, crystallises from hot water in thin white laminae which in the moist state quickly turn brown in the light. The *lead salt*, $(C^4H^7O^3)^2Pb + H^2O$, crystallises from water, in fine white translucent prisms. The *barium salt*, $(C^4H^7O^3)^2Ba + H^2O$, forms thick transparent prisms. The *sino salt*, $(C^4H^7O^3)^2Zn$, when freshly prepared, crystallises from hot water in fine pearly laminae, which gradually lose water when dried by heat, or over sulphuric acid, and yield an insoluble basic salt.

The *copper salt* forms fine green laminae; the *sodium salt* a granular crystalline mass; both are easily soluble in water and alcohol.

Trichlorobutyric Acid, $C^4H^3Cl^3O^2$ (K. Garzarolli-Thurnlak, *Liebig's Annalen*, clxxxii. 181). This acid is obtained by passing chlorine into the hydrate of butyric chloral (see *CHLORALS*) mixed with twice its weight of warm water, or by heating the same hydrate with potassium chlorate and hydrochloric acid:



It is identical with the acid (described as trichlorocrotonic acid, *2nd Suppl.* 396) which Judson obtained by the action of nitric acid on hydrate of butyric chloral (the so-called crotonic chloral, p. 50). When purified by washing with water, it forms an oil which does not solidify, even after standing over sulphuric acid for several days. It solidifies in a freezing mixture, but is liquefied again by very small quantities of water. It does not distil without alteration. The *lead salt*, $(C^4H^3Cl^3O^2)^2Pb$, obtained by neutralising the ethereal solution of the acid with lead carbonate crystallises, by spontaneous evaporation of the ethereal solution, in geodes having a silky lustre; from water in small shining needles. It dissolves also in alcohol. The crystals (contrary to Judson's statement) are anhydrous. The *calcium salt*, $(C^4H^3Cl^3O^2)^2Ca$, obtained in like manner, crystallises by very slow evaporation of the dilute ethereal solution, in geodes, otherwise as a soft white mass; it dissolves easily in water, alcohol, and ether. The *ammonium salt*, $C^4H^3(NH^4)Cl^3O^2$, prepared from the lead salt with ammonium carbonate, separates from water in tufts of crystals; it is less soluble in ether than in water or alcohol.

When trichlorobutyric acid is heated with caustic potash to 100° for several hours, a small quantity of a substance having the properties of dichlorocrotonic acid is formed, apparently by removal of the elements of hydrochloric acid.

Cyanobutyric Ether. An ethylic cyanobutyrate is obtained, together with the compound $HgK^2Cy^2Br^2$, by heating an alcoholic solution of pure ethylic bromobutyrate (b. p. 177.9° - 178.8° corr.) with potassio-mercuric cyanide to 180° . It is a colourless liquid, having an aromatic and spicy odour, and boiling at 208.4° - 209.4° (corr.), under a pressure of 762 mm. Its sp. gr. is 1.009 at 0° , less than 1 at ordinary temperatures. Ethylic bromisobutyrate (b. p. 163.6° corr.), treated in like manner, does not appear to yield a cyanisobutyric ether (Markownikoff, *Liebig's Annalen*, clxxxii. 324).

Oxybutyric Acids, $C^4H^7(OH)O^2$.—*a. Oxybutyric acid*, $CH^3.CH^2.CHOH.CO^2H$, is formed by the action of hydrocyanic and hydrochloric acids on propionic aldehyde (Prschibitesk, *Deut. Chem. Ges. Ber.* ix. 1312).

Oxidation.—According to Markownikoff (*Liebig's Annalen*, clxxvi. 309), *a*-oxybutyric acid is converted by oxidation into propionic and acetic acids. This is contrary to the general law respecting the oxidation of oxy-acids of the fatty series deduced by Ley a. Popoff (*ibid.* clxxiv. 61) from their experiments on the oxidation of oxyisovaleric acid, according to which all the oxyacids of the formula $R.CHOH.CO^2H$ yield, by oxidation, carbonic anhydride and a fatty acid, $C^2H^5O^2$, containing one carbon-atom less than the oxy-acid. According to this law, *a*-oxybutyric acid should yield by oxidation, only propionic acid. The simultaneous formation of acetic acid observed by Markownikoff is attributed by Popoff to the presence of *β*-oxybutyric acid, $CH^3.CHOH.CH^2.CO^2H$, a supposition rendered probable by the fact above mentioned, that the action of bromine on butyric acid gives rise to the simultaneous formation of *α*- and *β*-bromobutyric acid.

Methyl- and Ethyl-β-oxybutyric acids (Rohrbeck, *Liebig's Annalen*, lxxviii. 229; Waldschmidt, *ibid.* 240).

α-**Methyl-β-oxybutyric acid**, $CH^3.CHOH.CH(CH^3).CO^2H$, is formed (as sodium salt) by the action of water and sodium-amalgam on the ethylic ether of methyl-aceto-acetic acid:



the reaction being exactly similar to that by which *β*-oxybutyric acid is obtained from ethylic aceto-acetate (*1st Suppl.* 892).

The *sodium salt* thus obtained is, after purification, a white crystalline powder which melts above 240° to a clear liquid, turns brown and swells up when strongly heated, and may then be burned, with moderate facility, to sodium carbonate. The *silver salt*, $C^2H^5O^2Ag$, obtained by precipitating the sodium salt with silver nitrate, forms colourless laminae, nearly insoluble in cold, and only slightly soluble in boiling water.

The *free acid*, $C^8H^{10}O^2$, obtained by decomposing the sodium salt with sulphuric acid, and exhausting with ether, remains, on evaporation of the ether, in the form of a yellow syrup which cannot be made to crystallise, either by keeping it for months over sulphuric acid, or by cooling it to -20° , or by the use of any solvent whatever. When left over sulphuric acid, however, it becomes continually more viscid, and appears to be converted into an anhydride. By neutralisation with the carbonates of calcium, zinc, lead, &c., it yields salts which are almost uncrystallisable; those of the heavy metals are, moreover, easily decomposable, with formation of basic salts.

a-Methyl- β -Oxybutyric acid is resolved by distillation into water and methyl crotonic acid, $C^6H^8O^2$, the latter passing over as an oil which crystallises in the neck of the retort. The crystals melt at $62^\circ-62.5^\circ$, and exhibit all the other properties of the methyl-crotonic acid described by Frankland & Duppa (Rohrbeck).

a-Ethyl- β -Oxybutyric acid, $OH^1.CHOH.CH(C^2H^5).CO^2H$, obtained in like manner from the ethylic ether of ethyl-aceto-acetic acid, is a yellowish liquid, having a strong and disagreeably sour taste, miscible with water. When kept for some time in a dry vacuum, it does not crystallise, but becomes very viscid and appears to be partially converted into an anhydride. By distillation it is resolved into water and ethyl-crotonic acid, $C^6H^8O^2$.

The *sodium salt*, $C^8H^{11}NaO^2$, forms, after drying in a vacuum, a white fibrous crystalline mass, which deliquesces in moist air. The *silver salt*, $C^8H^{11}AgO^2$, is a white flocculent precipitate, which dissolves easily in boiling water, and separates on cooling in fine geodes of colourless laminae, which slowly become coloured on exposure to light. The *copper salt*, $C^8H^{11}CuO^2$, separates from a mixture of a concentrated solution of the sodium salt with cupric sulphate, slowly at ordinary temperatures, quickly on boiling, as a blue powder, the colour of which is finer and darker the more slowly the salt has separated (Waldschmidt).

BUXINE, $C^{16}H^{21}NO^2$. Barbaglia (*Deut. Chem. Ges. Ber.* iv. 767) prepares this alkaloid by exhausting the leaves and green branches of *Buxus sempervirens* with sulphuric acid, precipitating the acid solution with excess of carbonate of sodium or calcium, and exhausting the well-washed and dried precipitate with absolute alcohol. The alcohol having been distilled off, the residue is again treated with dilute sulphuric acid, and the parabuxine removed by Pavia's method. The buxine sulphate is then decomposed by excess of sodium carbonate and the well-washed precipitate is suspended in water, and dissolved by passing carbonic acid through the liquid. On boiling the resulting solution, a resin is precipitated, while buxine carbonate remains in solution, and from this solution the buxine may be precipitated perfectly white by ammonia.

Parabuxine, $C^{20}H^{25}N^2O$.—This alkaloid, discovered by Pavia, exists in *Buxus sempervirens*, together with buxine, and is distinguished therefrom by its lesser solubility in alcohol; it dissolves in hot alcohol, and separates on cooling as a white amorphous mass. Its *sulphate*, $C^{20}H^{25}N^2O.SO^2H^2$, obtained by neutralising the alkaloid with sulphuric acid, is more soluble in hot than in cold water, and is deposited in amorphous nodules insoluble in alcohol. The *hydrochloride*, $C^{20}H^{25}N^2O.2HCl$, prepared by boiling the sulphate with an excess of barium chloride, crystallises in minute needles. The *platinochloride*, $C^{20}H^{25}N^2O.2HCl.PtCl^4$, is amorphous. The *nitrate*, formed by decomposing the sulphate with barium nitrate, crystallises in scales (Pavesi & Rotondi, *Gazz. chim. ital.* iv. 192).

C

CABERITE. A variety of nickel-bloom first described and analysed in 1863 by H. Ferber (*Berg. u. Hüttenm. Zeitung*, 1863, 306), who found it to be a hydrated nickel-magnesium arsenate of the type $3\text{RO} \cdot \text{As}^2\text{O}^3 + 8\text{H}^2\text{O}$. This result is confirmed by Frenzel (*Jahrbuch f. Mineralogie*, 1874, 673), who finds the mineral to contain—

As^2O^3 .	NiO .	CoO .	MgO .	H^2O .	
41.42	25.03	1.49	6.94	25.78	100.66

corresponding with the formula $3(\text{NiO}, \text{MgO})\text{As}^2\text{O}^3 + 8\text{H}^2\text{O}$.

Caberite has an apple-green colour, crystallises in the monoclinic system, exhibits the forms of cobalt-bloom, and agrees in its cleavage with the latter and with gypsum. It differs from cobalt-bloom in giving off the whole of its water at 400° , whereas cobalt-bloom gives off only 20 per cent. of its water at that temperature, the rest at a red-heat. The ignited mineral is sometimes smalt-blue, sometimes bluish-black.

CACAO. See THEOBROMA.

CADMIUM. This metal may be obtained by distillation in a current of hydrogen, in regular octohedrons, dodecahedrons, &c., 6–8 m.m. long, with silver-white colour and strong refracting power (H. Kämmerer, *Deut. Chem. Ges. Ber.* vii. 1724).

Detection by the Blowpipe in presence of Zinc.—The substance to be tested, if in the metallic state, must be roasted, the resulting powder fused with borax, and acid sulphate of potassium added; the bead is then treated with boiling water, and a bead of potassium sulphide, prepared by heating acid sulphate of potassium on charcoal, is added; if cadmium be present, a yellow precipitate is formed (E. J. Chapman, *Chem. News*, xxxv. 13).

Estimation.—An elaborate paper on the quantitative estimation of cadmium has been published by O. Follenius (*Zeitschr. anal. Chem.* 1874, 272, 411), in which three methods of estimation are examined, viz., as sulphate, as oxide, and as sulphide.

1. *As Sulphate.* This method of estimation is regarded by Follenius as the most exact of all, provided it be carried out with the following precautions as to evaporation, drying, and weighing:—The perfectly pure solution of cadmium sulphate is to be evaporated in a weighed platinum dish, first over the water-bath as long as any vapours are thereby driven off. If the solution contains free sulphuric acid, it deposits during this evaporation crystals of the monohydrate $\text{CdSO}_4 + \text{H}^2\text{O}$. The free sulphuric acid is next to be carefully driven off on the sand-bath till the salt appears perfectly dry.

It is best to immerse the dish to the rim in a layer of sand of uniform thickness, and heat the bath over a large flame till the commencement of the evaporation, afterwards with only a small flame. The acid then goes off quietly and without bumping, and there is no fear of loss. The apparently dry mass usually still retains a small quantity of sulphuric acid, which must be expelled by heating over an open flame as long as white fumes are evolved: the remainder may then be left to cool in the exsiccator, and weighed. This first weighing gives the amount of sulphate to within 0.5–1.0 mgm. The weighed salt is then to be moistened with a few drops of dilute sulphuric acid, this acid expelled as before, and the dish, after cooling in the exsiccator, re-weighed.

By evaporation with excess of sulphuric acid as above described, all cadmium compounds containing volatile acids may be converted into sulphate. If, however, the salt is contaminated with ammonium chloride, this compound must be converted into sulphate by repeated evaporation with sulphuric acid, and the excess of acid finally driven off by ignition. In this manner the cadmium salt may be completely converted into sulphate, whereas, if cadmium sulphate is ignited with ammonium chloride or a fixed alkaline chloride, without the presence of free sulphuric acid, a double decomposition takes place, resulting in the formation of ammonium sulphate and cadmium chloride, which volatilises and occasions loss.

2. *As Oxide.* In weighing cadmium as oxide, regard must be had to the manner in which the oxide has been obtained, viz. (1) by ignition of the nitrate, or (2) by precipitating the nitrate, or (3) the sulphate or chloride, with an alkaline hydrate or carbonate. In the first two cases accurate results may be obtained after the first ignition; but in the third case the precipitate will be contaminated with potassium and sodium salts, which can be removed only by repeated washing and ignition. The

washing is best effected on an asbestos filter, as the oxide is easily reduced during ignition by adhering organic matters.

Tartaric acid prevents the precipitation of cadmium by the fixed alkalis completely in the cold; but the whole of the cadmium is precipitated by boiling. Citric, oxalic, succinic, and benzoic acids do not interfere with the precipitation, either from cold or from warm solutions. The presence of sugar completely prevents the separation of the hydrate at any temperature.

The precipitated cadmium carbonate, like the oxide, contains occasionally salts of the alkalis, and, except when obtained from the nitrate, must be repeatedly washed and ignited before it can be weighed. The salts of the fixed alkalis dissolve traces of the carbonate, which is also somewhat soluble in tartaric, oxalic, succinic, and benzoic acids, and to a greater extent in solution of sugar.

To convert the carbonate into the oxide, it is best to heat it together with the asbestos filter in a continuous current of air. If the heating be effected in a crucible, some metallic cadmium is formed and volatilised.

3. As Sulphide, CdS. Cadmium may be precipitated as sulphide either by hydrogen sulphide or by alkaline sulphides, but in the latter case the precipitate is very bulky and difficult to filter. The precipitate thrown down by hydrogen sulphide from a solution of sulphate or chloride of cadmium, carries down with it certain quantities of these salts,—from 0·943 to 2·107 per cent. in the case of the sulphate, and a larger quantity in the case of the chloride—which cannot be removed by washing. The adhering sulphate may however be completely converted into sulphide by ignition in a stream of hydrogen sulphide; the chloride, on the other hand, cannot be entirely converted into sulphide in this way: it is best therefore to precipitate from a solution of the sulphate.

The washing of the sulphide is best effected, like that of the oxide, on an asbestos filter, after which the precipitate may be dried by placing the asbestos tube in an air-bath gradually heated to 110°, and passing a current of air through it from the wide to the narrow end. The final ignition is also to be commenced towards the wide end.

Haloid Salts.—The solubility of several double haloid salts of cadmium in water, alcohol, and ether, has been determined by J. M. Eder (*Chem. Centr.* 1876, 615).

	Solubility			
	Water.	Alcohol. 0·794 sp. gr.	Ether. 0·729 sp. gr.	eq. vols. of alcohol and ether
2NH ⁺ Br.2CdBr ⁻ .H ⁺ O	0·73	5·3	280	24
4NH ⁺ Br.CdBr ⁻	0·96		decomposed	
2NaBr.2CdBr ⁻ .5H ⁺ O	1·04	3·7	190	—
4KBr.CdBr ⁻	1·40		decomposed	
KBr.CdBr ⁻ .H ⁺ O	0·79		decomposed	
2NH ⁺ ·1.2CdI ⁻ .H ⁺ O	0·60	0·88	2·4	—
2NH ⁺ ·1.CdI ⁻ .2H ⁺ O	0·53	0·70	8·9	1·8
2NaI.CdI ⁻ .6H ⁺ O	0·63	0·86	10·1	—
KI.CdI ⁻ .H ⁺ O	0·94	—	—	—
2KI.CdI ⁻ .2H ⁺ O	0·73	1·4	24·5	4·6

Phosphides.—The compounds Cd³P² and CdP² are obtained by passing phosphorus vapour over red-hot cadmium or its oxide or carbonate. The former has a metallic aspect, like that of the corresponding zinc-compound, and dissolves in dilute acids, with evolution of non-spontaneously inflammable phosphoretted hydrogen, and formation of hypophosphorous acid, cadmium chloride, and a yellow phosphoretted body—perhaps PO⁺OH (B. Renault, *Compt. rend.* lxxvi. 283).

CÆSIUM and RUBIDIUM. *Atomic Weights.*—A new determination of these weights has been made by Godeffroy (*Liebig's Annalen*, clxxxi. 176). Of the several methods proposed for the separation of caesium, rubidium, and potassium, he gives the preference to that of Hedenbacher, which consists in preparing the alums and separating these by fractional crystallisation. 100 parts of water dissolve at 17° of:

Potassium-alum.
13·5

Rubidium-alum.
2·27

Caesium-alum.
0·619

By a continual methodical fractionation the following crystallisations were obtained:

Pure caesium-alum.
The same, containing traces of rubidium.
Rubidium-alum with traces of caesium.
Pure rubidium-alum.
The same, with traces of potassium.
Potassium-alum with traces of rubidium.

The pure alums were converted into the pure chlorides by precipitating their hot solutions with pure ammonia, evaporating the filtrate in a platinum basin, igniting the residue, dissolving the fused mass in water, and adding pure barium chloride as long as a precipitate was formed. After filtering, pure ammonia and ammonium carbonate were added to the warm solution, and after standing for some time, the solution was again filtered, evaporated, and fused. This process was repeated, and then the chlorides crystallised. The pure caesium chloride thus obtained was not at all deliquescent, and the determination of chlorine gave, as mean of four very nearly agreeing results, the atomic weight of caesium = 132.557 (if Cl = 35.46 and Ag = 107.94), while that of rubidium was found = 85.476 as mean of four experiments.

On the Separation of Cæsium and Rubidium, see further p. 369.

On the Preparation of Cæsium from Lepidolite, see Sharples (*American Chemist*, iii. 453; *Jahresb. f. Chem.* 1873, 248).

Double Chlorides (Godeffroy, *Deut. Chem. Ges. Ber.* vii. 375; viii. 9).—When a solution of a caesium salt is added to a solution of *antimonious chloride* in concentrated hydrochloric acid, a white crystalline precipitate is obtained, consisting of a double chloride, $\text{SbCl}^3.6\text{CsCl}$. The formation of this precipitate is not prevented by the presence of the other alkalis. It may be collected, washed with strong hydrochloric acid, and crystallised from dilute hydrochloric acid. It then forms large tabular crystals, belonging to the hexagonal system, and permanent in the air. Antimonious chloride may therefore be used as a test for caesium.

The chlorides of several other metals likewise form with caesium chloride, crystalline precipitates which are only sparingly soluble in strong hydrochloric acid: viz. :—

$\text{Fe}^2\text{Cl}^6.6\text{CsCl}$	$\text{HgCl}^2.2\text{CsCl}$
$\text{BiCl}^3.6\text{CsCl}$	$\text{CuCl}^2.2\text{CsCl}$
$\text{ZnCl}^2.2\text{CsCl}$	$\text{MnCl}^2.2\text{CsCl}$
$\text{CdCl}^2.2\text{CsCl}$	$\text{NiCl}^2.2\text{CsCl}$

To obtain these precipitates, the chlorides of the corresponding metals must be dissolved in strong hydrochloric acid, and the solution mixed with a solution of caesium chloride also in strong hydrochloric acid. They are all extremely soluble in dilute hydrochloric acid and in water, but crystallise again from the solutions on evaporation.

By mixing a solution of rubidium chloride with the chlorides of the several metals above mentioned, well-crystallised double salts are obtained analogous in composition in every case to the corresponding caesium salts, e.g. $\text{SbCl}^3.6\text{RbCl}$, $\text{Fe}^2\text{Cl}^6.6\text{RbCl}$, $\text{ZnCl}^2.2\text{RbCl}$, &c.

The following table gives a comparative view of the reactions of caesium and rubidium chloride with the chlorides of the metals above mentioned and with platonic chloride: it will be seen that caesium chloride gives a precipitate in every case; rubidium chloride in six only:

	CsCl	RbCl
Antimonious chloride	white	no pp.
Bismuthous "	white	"
Ferric "	orange-red	"
Zinc "	white	"
Cupric "	red	red
Manganous "	pale rose-red	pale rose-red
Nickel "	yellow	turbidity
Platinic "	yellow	yellow
Stannic "	white	white

With the exception of platonic chloride, however, none of these reagents can be used for the quantitative separation of caesium from the other alkali-metals, inasmuch as the precipitates are formed only in strongly acid solutions, and disappear on dilution or on prolonged washing.

The picrates of caesium and rubidium resemble potassium picrate in being sparingly soluble in water, very sparingly in alcohol.

Separation of Cæsium and Rubidium.—Traces of rubidium may be removed from cæsium-alum by converting this salt into the chloride, dissolving the latter in strong hydrochloric acid, and precipitating with an acid solution of antimonious chloride. The precipitate, after being washed with hydrochloric acid, is free from rubidium. On treating it with water, antimony oxychloride separates out: if the solution is evaporated and ignited with sal ammoniac, all the remaining antimony volatilises and pure cæsium chloride is left behind.

On treating rubidium-alum containing cæsium in a similar way, the precipitate obtained contains traces of rubidium, which may be removed by dissolving in dilute hydrochloric acid and precipitating again by the concentrated acid.

Other chlorides of the heavy metals, as already observed, also give precipitates with cæsium chloride in presence of strong hydrochloric acid, and the sulphate is precipitated by the sulphates of these metals when dissolved in dilute sulphuric acid; potassium and rubidium salts do not give this reaction.

CAFFEINE. For the rapid extraction of caffeine (theine) from tea, the following method is recommended by Cazeneuve et Caillol (*Bull. Soc. Chim.* [3], xxvii, 199). Black tea is treated with four times its weight of boiling water, and when the leaves are softened, an amount of freshly slaked lime, equal to the weight of tea originally taken, is added, and the whole well mixed and evaporated to dryness on a water-bath. The residue is then placed in an exhausting apparatus, and exhausted by means of chloroform; the extract thus obtained is evaporated to dryness; and the resinous matter is precipitated by treating the residue with boiling water. On carefully evaporating the filtered aqueous solution, beautiful silky white crystals of caffeine are obtained.

Detection.—According to Böttger (*Zeitschr. anal. Chem.* 1873, 442) caffeine may be detected by the purple-red coloration which ensues on extracting the substance under examination with alcohol, treating the dry extract with boiling hydrochloric acid, evaporating to dryness and redissolving in water.

Estimation.—R. Weyrich (*Zeitschr. anal. Chem.* 1873, 104) has examined the methods proposed by Mulder, Péligot, Claus, Zöller, and Lieventhal for the estimation of caffeine in tea and coffee.

Péligot's method (*Rep. Pharm.* Lxxii, 340) consists essentially in precipitating the tea-infusion with basic lead acetate, with addition of a very small quantity of ammonia, and after careful washing, decomposing the filtrate with sulphuretted hydrogen. After a second filtration, the caffeine crystallises out of the liquid. Any caffeine that remains in the mother-liquor is estimated by titration with tannin.

The objections to the method are that it requires a large amount of material to work with, and that the titration is untrustworthy, because the tannin carries down other matters beside caffeine, and thus gives results too large. On the other hand, it is possible that less than the real amount of caffeine may be obtained, because lead sulphide carries down with it such matters as alkaloids, and retains them when washed.

The method of Claus (*Jahresb.* 1863, 708) consists in exhausting the leaves with ether, shaking up the ethereal solution with water containing sulphuric acid, supersaturating the acid caffeine solution with calcined magnesia, evaporating to dryness, and exhausting the dried residue with ether. This method, which is very similar to Mulder's, gives tolerably uniform results. The source of error in it is that the whole of the caffeine is not always extracted in shaking up the first ethereal solution with water.

Zöller's method (*Jahresb.* 1871, 818) consists in boiling the powdered tea-leaves with common sulphuric acid a little diluted. Water is then added, and the liquid is neutralised with hydrated oxide of lead and evaporated to dryness, and the residue is exhausted with alcohol of 85 per cent. After filtration and evaporation to dryness, the caffeine is extracted with ether, and remains behind on evaporating the solvent. The caffeine thus obtained is, however, very impure, and besides it is not impossible that when thus heated for some time with an acid, it may be partly decomposed, and in that case the result will be below the real percentage.

Lieventhal (*Chem. Centr.* 1872, 631) boils the powdered tea for a minute or two with chloroform. After cooling, the mass is washed till the chloroform flows through colourless. The filtrate is distilled and the residue boiled with distilled water and evaporated to dryness. The caffeine then remains behind, but is not colourless. Weyrich is of opinion that the chloroform does not penetrate into the tea, even when finely powdered, sufficiently to extract all the caffeine; moreover, other substances, as well as the caffeine, pass into solution.

Mulder's method (*J. pr. Chem.* xv, 280) appears to be preferable to all others, on account of its simplicity, and more especially because the caffeine is obtained by it

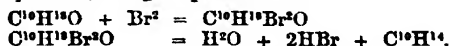
perfectly pure in colourless crystals. Raw coffee-berries are dried at 100° , and then finely powdered. Tea can be used just as it is found in commerce. A weighed quantity is boiled with distilled water: in the case of coffee three times, each of an hour's duration; in the case of tea, as long as the filtrate comes through coloured. By this means all the caffeine, as well as some other matters, passes into solution. The filtrate is evaporated on the water-bath to the consistence of a syrup, and then, after being mixed with calcined magnesia to strong alkaline reaction, evaporated to dryness. The finely powdered residue is digested for several days with ether, then filtered, and the residue is again treated with ether, and finally washed with ether upon the filter as long as a drop of the filtrate placed on a watch-glass leaves a residue of caffeine. The ether is then distilled off, and the pure caffeine remains. Weyrich prefers chloroform to ether, as caffeine is more soluble in the former, and the operation is thus shortened.

Solubility.—The solubility of caffeine in chloroform, alcohol, water, ether, carbon sulphide, and petroleum has been determined by Commaille (*Compt. rend.* lxxxi. 817) with the following results:—

	100 grams of liquid dissolve at 15° – 17° of Caffeine		Coefficient of solubility at 15° – 17° of Caffeine		100 grams of liquid dissolve at boiling heat of Caffeine		Coefficient of solubility at boiling heat of Caffeine	
	Hydrated	Anhydrous	Hydrated	Anhydrous	Hydrated	Anhydrous	Hydrated	Anhydrous
Chloroform . . .	—	12.97	—	$\frac{1}{7.72}$	—	19.02	—	$\frac{1}{5.25}$
Alcohol at 85° . .	2.51	2.30	$\frac{1}{40}$	$\frac{1}{44.4}$	—	—	—	—
Water* . . .	1.47	1.35	$\frac{1}{68}$	$\frac{1}{74.2}$	49.73	45.65	$\frac{2.01}{1}$	$\frac{1}{2.19}$
Alcohol, absolute . .	—	0.61	—	$\frac{1}{164.7}$	—	3.12	—	$\frac{1}{32}$
Ether of commerce . .	0.21	0.19	$\frac{1}{467}$	$\frac{1}{526}$	—	—	—	—
Sulphide of carbon . .	—	0.0585	—	$\frac{1}{1709}$	—	0.454	—	$\frac{1}{220}$
Ether, purified and anhydrous. }	—	0.0437	—	$\frac{1}{2288}$	—	0.36	—	$\frac{1}{277}$
Light petroleum . .	—	0.025	—	$\frac{1}{4000}$	—	—	—	—

* The water was at 65° only, and not boiling.

CAJEPUTOL, $C^{10}H^{10}O = C^{10}H^{10}.H^2O$. This compound is the chief oxidised constituent of oil of cajeput. When separated by distillation from a liquid resinous constituent, and purified by fractional distillation, it boils at 176° – 186° . It unites with bromine, the combination being attended with considerable rise of temperature; and the product, when distilled, gives off hydrobromic acid and yields a quantity of cymene equal to about two-thirds of the substance used, the calculated quantity, according to the following equations, being 87 per cent.:—



The cymene thus produced agrees in properties with that which is obtained from many other terpene derivatives (Wright & Lambert, *Chem. Soc. Jour.* 1874, 619). Compare 2nd Suppl. 419.

CALAMUS. The wood of the Spanish reed (*Calamus Rotang*) contains a large quantity of silica, and gives sparks with steel, or when two pieces of it are rubbed together. The reed dried at 100° yielded 3.16 per cent. of ash having the following composition:—

SiO ²	CaO	MgO	K ² O	Na ² O	Fe ² O ³	P ² O ⁵	SO ²
67.964	16.969	11.812	0.653	0.559	0.333	0.295	0.755 = 99.340.

These numbers agree very nearly with the formula of a calcium-magnesium silicate, $CaO.MgO.4SiO^2$, which requires 71.4 per cent. silica, 16.6 lime, and 11.8: (Mutscher, *Liebig's Annalen*, clxxvi. 86).

A telluride of gold and silver occurring, with sylvanite and red quartz, at Red Cloud Mine, Gold Hill, Boulder Co., Colorado. Two analyses gave the following results:—

Au	Ag	Te*	Cu and Fe
40.59	2.24	57.67	trace = 100.50
39.76	2.56	57.68	— = 100.00

(F. A. Genth, *J. pr. Chem.* [2], x. 355).

CALCITE or CALOSPAR. On the crystalline form of calcite from Rodefjord, Iceland, see Hessenberg (*Jahrb. f. Min.* 1873, 87); from Schneeberg in Saxony: Frenzel and vom Rath (*ibid.* 1875, 415); from Andreasberg: Hessenberg (*ibid.* 1875, 647); from Russia: v. Kokscharow (*ibid.* 1875, 873; *Chem. Soc. Jour.* 1875, i. 525).

On Hemimorphism in Calcite: Frenzel (*Jahrb. f. Min.* 1875, 673; *Chem. Soc. Jour.* 1875, j. 50); also Max Bauer (*Jahrb. f. Min.* 1873, 190).

On the appearances produced in Calcite by pressure: Reusch, *Pogg. Ann.* cxlvii. 307).

CALCIUM. *Volatility at High Temperatures.*—Calcium may be volatilised in the same manner as barium, viz. by intense ignition of its oxide in a wind-furnace in contact with aluminium (Mallet, p. 142).

On the Spectrum of Calcium at very high temperatures, see SPECTRAL ANALYSIS.

Separation from Magnesium.—Sonstadt (*Chem. News*, xxix. 209) recommends* for this purpose the use of *potassium iodate*. When calcium is precipitated as oxalate in the usual way from a solution containing calcium and magnesium, it is well known that a certain portion of magnesium always accompanies the calcium precipitate. Besides this, however, calcium is not completely precipitated under such circumstances, a certain quantity being held in solution by the influence of the magnesium salts. Sodium tungstate effects a more complete separation, but the solution must be quite neutral, and other alkaline salts absent or nearly so. Under these circumstances calcium is very completely thrown down, and the precipitate is quite free from magnesium. But even after separating the tungsten as completely as possible, the magnesium precipitate, obtained with alkaline phosphate and ammonia, is still found to contain tungsten.

Now calcium iodate is not sensibly soluble in a saturated solution of potassium iodate, whilst magnesium is not precipitated from solution in any degree by potassium iodate. The presence of potassium iodate does not interfere with the subsequent precipitation of the magnesium as magnesium-ammonium phosphate, the double phosphate being less soluble in a saturated solution of potassium iodate containing free ammonia, than in a mixture of 2 pts. of ordinary aqueous ammonia with 1 pt. water. Potassium iodate solution added to the supernatant liquid containing alkaline phosphate and much free ammonia overprecipitated magnesium-ammonium phosphate, renders the liquid opalescent, and causes a further precipitation of magnesium salt.

On the detection of Phosphate and Oxalate of Calcium, &c. in the Ammonium Sulphide Group, see Hilger (*Zeitsch. anal. Chem.* 1874, 133; *Chem. Soc. Jour.* 1874, 102).

Chloride, CaCl².—This salt forms the chief saline constituent of a black slimy exudation occurring on the face of the old red sandstone rocks at Guy's Cliff in Warwickshire. The composition of this black slime is as follows:

CaCl ²	CaSO ⁴	Ca(NO ³) ²	MgCl ²	KCl	NaCl	X*
27.15	12.55	trac*	3.81	1.21	11.03	42.25 = 100

The sand-stone rock, containing 95.64 per cent. sand and mica, 1.24 alumina, ferric oxide, &c., 2.00 calcium carbonate, 0.66 magnesium carbonate, and 0.46 moisture, &c. does not afford the material for the formation of this deposit; nevertheless it is always present, and, if washed away by the rains, is continually renewed. This would seem to indicate the existence of hidden salt-beds in the neighbourhood (J. Spiller, *Chem. Soc. Jour.* 1876, i. 154).

Calcium chloride occurs, together with magnesium chloride and alkaline chloride, in the tachydrite and carnallite of the Stassfurt deposit, but in smaller proportion than the Guy's Cliff exudation, tachydrite containing 21 per cent. CaCl² and 36 per cent. MgCl²; carnallite about 8 per cent. CaCl² and 31 per cent. MgCl².

Oxychloride.—According to Grimshaw (*Chem. News*, xxx. 280) the salt which separates out in slender, white, needle-shaped crystals when a strong solution of calcium chloride is boiled with an excess of milk of lime yields, on analysis, numbers

* Water and vegetable extractive matter.

corresponding with the formula, $3\text{CaO} \cdot \text{CaCl}^2 + 15\text{H}^2\text{O}$, or $\text{CaOH} \cdot \text{CaCl} + 7\text{H}^2\text{O}$. Rose assigned the formula $3\text{CaO} \cdot \text{CaCl}^2 + 16\text{H}^2\text{O}$, but his numbers agree better with the above formula. The salt is stable out of contact with air; loses part of its water of crystallisation over sulphuric acid or quick lime, and absorbs water and carbonic acid from the air.

Peroxide, CaO^2 .—This compound is most conveniently prepared by adding lime-water in considerable excess to an aqueous solution of sodium peroxide acidulated with nitric acid; it then separates in crystalline scales, having the composition $\text{CaO}^2 \cdot 8\text{H}^2\text{O}$. The same hydrate is obtained as a very finely divided white precipitate on adding a neutral or alkaline solution of sodium peroxide to a solution of a calcium salt (Conroy, *Chem. Soc. J.* 1873, 810). It is isomorphous with hydrated barium dioxide (p. 142).

Basic Sulphocarbonate.—Milk of lime agitated with carbon disulphide yields bright orange needles of the compound $\text{CaCS}^2 \cdot \text{CaH}^2\text{O}^2 + 6\text{H}^2\text{O}$, similar in properties to the corresponding barium compound (p. 142).

CALDEIRAS. This name is applied to the geysers of the Furnas valley in the island of San Miguel, Azores. See GEYSERS, 2nd Suppl. 553.

CALDONITE. According to the earlier analyses of Brooke and Thomson, this mineral, from Leadhills in Scotland, was regarded as a sulphatocarbonate of lead mixed with cupric oxide or carbonate (i. 722); but according to Maskelyne & Flight (*Chem. Soc. J.* 1874, 101) the carbonic acid is due to accompanying cerussite; and, this being deducted, the mineral is found to contain 17·30 per cent. SO^2 , 68·42 PbO, 10·17 CuO, and 4·05 H^2O , agreeing nearly with the formula $5\text{PbSO}^4 \cdot 2\text{PbH}^2\text{O}^2 \cdot 3\text{CuH}^2\text{O}^2$, or 3 mols. linarite, 2 mols. lanarkite, and 2 mols. water (calc. 19·14 SO^2 , 65·17 PbO, 11·39 CuO, and 4·30 aq.)

CALISAYA. On the alkaloids of Javanese Calisaya bark, see Hesse (*Livbig's Annalen*, clxiv. 337; *Chem. Soc. J.* 1875, 282); and de Vrij (*Pharm. J. Trans.* [3], v. 501; *Chem. Soc. J.* 1875, 184).

CAMPHENES. See TERPENES.

CAMPIC ACID

camphor with alcoholic potash (i. 720), is also formed by the action of oxygen on sodium-camphor: $\text{C}^{10}\text{H}^{15}\text{NaO} + \text{O} = \text{C}^{10}\text{H}^{13}\text{NaO}^2$. To prepare it, the product of the action of sodium on camphor is dissolved in coal-tar naphtha boiling at 125° , and a current of air is passed through the gently-boiling liquid. After the reaction is finished, the naphtha is distilled off, the residue exhausted with water, and the solution fractionally precipitated with an acid. First a resin is precipitated carrying down camphoric acid, which is also formed, and then camphic acid is thrown out, while some camphoric acid remains in solution.

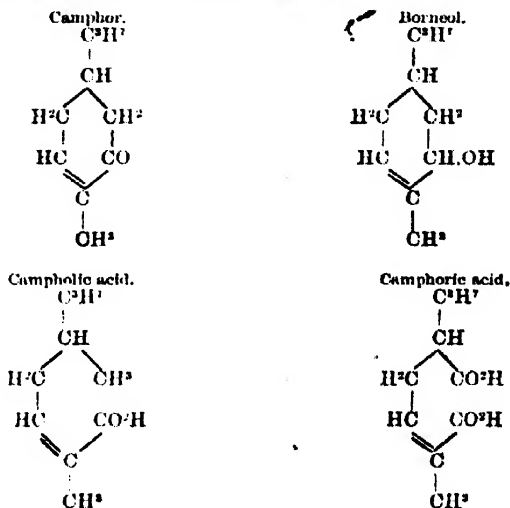
Camphic acid yields, by double decomposition with copper salts, the salt $(\text{C}^{10}\text{H}^{13}\text{O}^2)\text{Cu}$ as a green powder, which is partly soluble in ether, benzene, chloroform, and strong alcohol. The green alcoholic solution deposits a viscid almost black mass, drying up to a dark-green brittle substance consisting of $\text{C}^{10}\text{H}^{13}\text{O}^2 + (\text{C}^{10}\text{H}^{13}\text{O}^2)_2\text{Cu}$.

By oxidising camphic acid with potassium permanganate, it is converted into oxycamphic acid, $\text{C}^{10}\text{H}^{13}\text{O}^3$, which does not crystallise, and resembles camphic acid, but is more liquid. At the same time some acetic acid and camphoric acid are formed, as well as an acid which appears to be toluic acid (Montgolfier, *Bull. Soc. Chim.* [2], xxv. 13).

CAMPHOCARBONIC ACID, $\text{C}^{11}\text{H}^{15}\text{O}^3 = \text{C}^{10}\text{H}^{13}\text{O} \cdot \text{CO}^2\text{H}$, obtained by the action of carbon dioxide on sodium-camphor (1st Suppl. 385), is converted, by the action of bromine, so regulated as to avoid rise of temperature, into a yellowish mass, which gradually becomes crystalline and dissolves completely in dilute alkalis, the solution yielding with hydrochloric acid—immediately or after some time, according to the degree of dilution—a white crystalline precipitate of monobromocamphocarbonic acid, $\text{C}^{10}\text{H}^{13}\text{BrO}^2$. This acid melts at 109° – 110° , dissolves sparingly in water, easily in alcohol and ether. It is very easily resolved, in the dry state at 65° , or in alcoholic solution on boiling, into CO^2 and bromocamphor (m. p. 76°). Its salts decompose in the same manner, those of the alkali metals even when evaporated over sulphuric acid, the barium salt when its aqueous solution is boiled. The salts $(\text{C}^{10}\text{H}^{13}\text{BrO}^2)_2\text{Ba}$ and $\text{C}^{10}\text{H}^{13}\text{BrO}^2\text{Ag}$ may however be obtained, as crystalline precipitates, by treating the corresponding acetates with an ammoniacal solution of bromocamphocarbonic acid (J. de Santos de Silva, *Deut. Chem. Ges. Ber.* vi. 1092).

CAMPHOCREASOTE. See OXYCENE, under CYMENE.

CAMPHOR, $C^{10}H^{16}O$. This body has been variously regarded as an alcohol, a phenol, an aldehyde, and a ketone, the last view being at present most generally accepted, and several constitutional formulæ have accordingly been proposed for it (2nd Suppl. 234), neither of them, however, being capable of affording a complete explanation of all its reactions. To this end, it must be remembered in the first place that camphor is an indifferent body; secondly, that by combining with hydrogen, it is converted into borneol, which possesses the character of an alcohol; thirdly, that alkalis transform it into monobasic campholic acid, and oxidising agents into bibasic camphoric acid. It must also be remembered that, by abstraction of the elements of water, camphor is readily converted into cymene, an aromatic hydrocarbon, containing methyl and propyl (or isopropyl) in the para-position. All these reactions are readily explained by the following formulæ;—



In assuming these formulæ, it must be stated that the positions of the radicals, CH^2 and C^2H^2 , are known, but those of the oxygen and of the double-linked carbon-atoms must at present be left undecided.

Camphor is therefore a kind of ketone, and borneol the corresponding secondary alcohol, the formation of which from camphor is similar to that of other secondary alcohols from their ketones, although it takes place under somewhat different conditions. In the formation of campholic acid and camphoric acid, the linking C^2H^2 carbon-atoms is severed, that which was combined with oxygen being converted into carboxyl, while the other combines with hydrogen, under the influence of alkalis, and is converted into carboxyl under the influence of oxidising agents.

The transformation of camphor into cymene is a complicated reaction, intermediate products being formed, varying with the dehydrating agent used. Such a compound is thio-cymene, which is produced by the action of phosphorus pentasulphide (Kekulé, *Deut. Chem. Ges. Ber.* vi. 929).

On the Constitution and Chemical Function of Camphor, see also Berthelot, *Compt. rend.* lxxix. 1093; *Chem. Soc. J.* 1875, 348.

Optical Rotatory Power.—The specific rotatory power of camphor has been determined by Landolt (*Deut. Chem. Ges. Ber.* ix. 914). The camphor employed was purified by sublimation; it boiled at 204° and solidified at 175° . Its rotatory power was determined by dissolving it in various proportions of each of the undermentioned liquids, and observing the rotation produced by the solutions at 20° . It was found that, with all the solvents except the last two, the rotatory power of the camphor in solution could be expressed by the formula $[\alpha] = A - Bq$ (A and B being constants, and q the percentage of solvent in the solution); that is to say, the alteration produced in the normal rotatory power of pure camphor by these solvents was proportional to the amount of the solvents present, so that A represents the true rotatory power of camphor. With the last two solvents, however, it was found possible to express the rotation only by the more complicated formula $[\alpha] = A - Bq + Cq^2$.

The following are the solvents used and the formulæ arrived at:—

Acetic acid	$[\alpha] = 55.49 - 0.13729 q$;
Ethyl acetate	$[\alpha] = 55.15 - 0.04383 q$;
Ethyl monochloracetate	$[\alpha] = 55.70 - 0.06685 q$;
Benzene	$[\alpha] = 55.21 - 0.1630 q$;
Dimethylaniline	$[\alpha] = 55.78 - 0.1491 q$;
Wood-spirit	$[\alpha] = 56.15 - 0.1749 q + 0.0006617 q^2$
Alcohol	$[\alpha] = 54.38 - 0.1614 q + 0.000369 q^2$.

Calculating from these formulæ the value of $[\alpha]$ for the limits $q=0$ and $q=100$ the following numbers are arrived at:—

Solvent.	$[\alpha]$ for $q=0$. Pure camphor.	$[\alpha]$ for $q=100$. Infinite dilution.	Total alteration.
Acetic acid	55.5	41.8	13.7
Ethyl acetate	55.2	50.8	4.4
Ethyl monochloracetate	55.7	49.0	6.7
Benzene	55.2	38.9	16.3
Dimethylaniline	55.8	40.9	14.0
Wood-spirit	56.2	45.3	10.9
Alcohol	55.4	41.9	12.5

The mean of the values thus obtained for the pure substance gives for the specific rotatory power of camphor at 20° —

$$[\alpha]_D = 55.6^\circ \mp 0.4^\circ.$$

See also Montgolfier (*Bull. Soc. Chim.* [2], xxii. 487).

On the movements of Camphor on Water and other Liquids, see Tomlinson (*Phil. Mag.* [4], xlv. 376; *Pharm. J. Trans.* [3], iv. 654, 672).

Influence of Camphor on Vegetation.—According to A. Vogel a. L. Raab (*Pharm. J. Trans.* [3], iv. 1014), the growth of many plants is promoted by camphor, whereas on others it exerts either a deleterious influence or none at all. It accelerates the germination of seeds. A similar influence is exerted by water containing oil of turpentine.

Action of Heat.—During the sublimation of camphor, a quantity of oily liquid drops from the mass, resolvable by fractional distillation into a hydrocarbon of the terpene group, a body having the composition of a terpene hydrate, $C^{10}H^{18}O$, and a liquid oil containing less oxygen than camphor, together with much ordinary camphor (Beckett a. Wright, *Chem. Soc. Jour.* 1876, i. 7).

Reaction with Benzyl Chloride and Zinc-dust.—When camphor is heated with benzyl chloride and zinc-dust, a violent action takes place attended with evolution of hydrochloric acid. The product, when distilled, freed from hydrochloric acid and water, and again distilled, yields a viscid mass enclosing a crystalline substance, and a liquid which, by repeated fractionation, may be resolved into six portions boiling respectively at 110° – 112° , 161° – 162° , 162° – 164° , 176° – 178° , 189° – 190° , and 203° – 204° . The first is toluene, C^7H^8 ; the second a hydrocarbon, $C^{10}H^{14}$ or $C^{10}H^{16}$; and the last three are oxygenated bodies, $C^7H^{10}O$, $C^{10}H^{14}O$, $C^{10}H^{16}O$. The fraction boiling at 162° – 164° is probably a mixture (Tommasi, *Bull. Soc. Chim.* [2], xxi. 400, 451).

Conversion of Camphor into a Terpene (J. Riban, *Ann. Chim. Phys.* [5], vi. 378).—The camphor is first converted into borneol, $C^{10}H^{18}O$, by the action of sodium (1st *Suppl.* 358); the borneol thus obtained ($[\alpha]_D = +2.6$) is transformed, by heating to 100° with fuming hydrochloric acid, into the hydrochloride $C^{10}H^{18}.HCl$, which is optically inactive, resembles ordinary terebene hydrochloride, melts in an atmosphere of hydrogen chloride at 145° , and is decomposed by water, slowly at ordinary temperatures, quickly when heated to 100° , with formation of a hydrocarbon, $C^{10}H^{16}$, called by Riban, *Borneo camphene* (see TERPENES).

Conversion of Terpene into Camphor.—Terebenthene, the levorotatory terpene obtained from French turpentine oil (v. 921), is oxidised to camphor by boiling it for fifteen hours with chromic acid mixture, acetic acid and a small quantity of butyric acid being formed at the same time. The camphor is purified by distillation in a current of steam, washing with potash-ley, pressure, fractional distillation, and sublimation with lime at 100° . Any traces of the terpene that remain may be removed by fractional sublimation, rejecting the first sublimate; if the camphor still retains bodies of higher boiling point, it must be dissolved in nitric acid, precipitated with water, and finally sublimed with lime. The camphor thus obtained has the pungent odour and other properties of ordinary camphor, but melts at a somewhat lower temperature (172° corr.) and is levorotatory; $[\alpha]_D = -13.7^\circ$. By oxidation with nitric acid it yields a camphoric acid, $C^{10}H^{16}O^2$, which is also levorotatory; $[\alpha]_D = -6.6^\circ$.

and melts at 197° – 198° (corr.); camphoric acid from laurel camphor melts at 187° (corr.) (Riban, *loc. cit.*)

Bromocamphors, $C^{10}H^{11}BrO$ and $C^{10}H^{11}Br^2O$ (1st Suppl. 387).—These compounds have been further examined by Montgolfier (*Bull. Soc. Chim.* [3], xxiii. 253).

Monobromo-camphor is but slightly soluble in alcohol, but very soluble in chloroform, carbon tetrachloride and benzene. It sublimes easily. When it is acted on by nascent hydrogen the original camphor is regenerated. This hydrogenation is most easily effected by a 2 per cent. sodium-amalgam in an alcoholic solution.

Dibromo-camphor is most easily prepared by heating 1 mol. of camphor and 4 of bromine in sealed tubes. A large quantity of some liquid body is produced at the same time, so that the dibromo-camphor does not always crystallise immediately. It is best to leave the liquid at rest until it solidifies; the yield is, however, small under all circumstances. This body does not sublime appreciably at 100° . It is less soluble in alcohol than monobromo-camphor, but dissolves in the solvents before mentioned, and presents generally the properties of the mono-brominated variety.

The bromo-derivatives of camphor unite with acids similarly to camphor itself, and a compound of monobromo-camphor with hydrobromic acid appears to be obtained in the preparation of the bromo-camphors, in the form of a viscous strongly acid liquid, which, when exposed on a capsule, gives off hydrobromic acid, while monobromo-camphor crystallises out.

The compounds $C^{10}H^{10}O.Br^2$ and $C^{10}H^{11}BrO.Br^2$ may also be formed; but they are very unstable and are decomposed during desiccation.

On Monobromo-camphor, see also Maisch (*Chem. Centr.* 1873, 437; *Chem. Soc. Jour.* 1874, 582).

Ledum Camphor. The leaves of the marsh wild rosemary (*Ledum palustre*) yield, by boiling with water, a volatile oil which soon becomes crystalline on exposure to the air. The camphor thus obtained is almost insoluble in water, but dissolves readily in alcohol, ether, and chloroform, from which solvents it separates in fine prismatic crystals which are coloured dark-violet by a drop of nitric or sulphuric acid, and yield orange-coloured crystals when boiled with nitric acid of sp. gr. 1.35. They give by analysis 83.4 per cent. carbon and 11.4 hydrogen from which J. Tropp (*Deut. Chem. Ges. Ber.* viii. 542) deduces the formula $C^{20}H^{20}O$, requiring 84 per cent. C. and 12 H. Wright, however, points out (*Chem. Soc. Jour.* 1876, 1038) that the analytical numbers agree better with the more probable formula $C^{20}H^{22}O$, which requires 83.3 C. and 11.1 H.

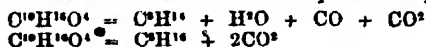
The oil is converted by chlorine into a black mass.

Anise Camphor. See ANETHOL, p. 85.

Isula Camphor. See INULOL.

Ngai Camphor. This camphor, obtained from China, sublimes in well-defined crystals resembling those of borneol, with which it is isomeric. It melts at 204° , has a sp. gr. of 1.02, and vapour-density 78.98 ($H=1$), agreeing with the molecular formula $C^{10}H^{14}O$ (calc. 77). Its odour is very much like that of ordinary camphor, but less powerful (S. Flowman, *Pharm. J. Trans.* [3], iv. 712).

CAMPHORIC ACID, $C^{10}H^{12}O^4 = C^5H^4(CO^2H)^2$ (Wreden, *Liebig's Annalen* clxxxvii. 156, 168; compare 2nd Suppl. 235). This acid, heated with hydrochloric or hydriodic acid, yields the hydrocarbons, tetrahydro-isoxylene, C^8H^6 , and hexhydro-isoxylene, C^8H^{10} , separate or mixed, according to the conditions of the experiment. The reactions by which these bodies are formed are represented by the equations:—



Pure hexhydroisoxylene may be obtained: (1). By heating 6 grams of camphoric acid to 280° in sealed tubes for about fifty hours with 30 c.c. of hydriodic acid

exhibits the composition C^8H^{10} , and when gently heated with twice its volume of a mixture of nitric and sulphuric acids is converted into trinitroisoxylene, $C^8H(NO^2)^3$.

(2). By heating 4 grams of camphoric acid to 200° for ten hours with 8 c.c. hydriodic acid of sp. gr. 1.7, washing the resulting heavy oil with water and again heating it for nine hours to 200° with hydriodic acid of the same strength.

Hexhydroisoxylene, mixed with a small quantity of the tetrahydro-compound, is obtained by heating 4 grams of camphoric acid to 130° with hydriodic acid saturated at 0° , and treating the resulting heavy iodated oil with alcoholic potash.

Tetrahydroisoxylene, mixed with a small quantity of the hexhydro-compound, is obtained: (1). By heating camphoric acid with hydriodic acid of sp. gr. 1.7, as in the

(2). By heating 7 grams of camphoric acid to 200° for ten or twelve hours, with about 15 c.c. of hydrochloric acid saturated at 0°, washing the product with aqueous sodium carbonate and with water, distilling, and treating the distillate with alcoholic potash, or distilling it over lime, to remove chlorine, and finally purifying it with sodium. The product thus obtained boils at 118°-122°.

The formation of tetrahydro-isoxylene by the action of HI or HCl on camphoric acid is preceded by the conversion of that acid into the optically inactive variety, *mesocamphoric acid* (2nd Suppl. 235): hence it appears probable that inactive camphoric acid is the dicarbon-acid of tetrahydro-isoxylene, and that the ordinary dextrogyrate acid stands in the same relation to the isomeric hydrocarbon C^8H^{14} boiling at 105° (Wreden).

CANTHARIDES. According to H. Poeklington (*Pharm. J. Trans.* [3], iii. 681) the extracts obtained by treating cantharides with alcohol, ether, and carbon sulphide, exhibit absorption-spectra agreeing with that of chlorophyll, whence it is probable that the colouring matter of cantharides is derived from the plants on which they feed.

The solubility of cantharidin in various liquids has been determined by Rennard with the following results:

	Per cent. of cantharidin dissolved.
Boiling water	0·290 — 0·297
Cold water	0·020
Boiling alcohol	2·030 — 2·168
Cold alcohol	0·127
Boiling benzin	3·38
Cold benzin	0·51
Hot hydrochloric acid (sp. gr. 1·17)	0·3
" " " " " "	0·137

On the decomposition of Cantharidin in Cantharides, see R. Wolff (*Arch. Pharm.* [3], x. 22; *Chem. Soc. J.* 1877, i. 722). •

CAOUTCHOUC. *Density.*—According to K. Puschl (*Chem. Centr.* 1875, 146), the density of caoutchouc attains a minimum at a certain temperature, which is lower as the mechanical stretching of the caoutchouc is greater.

Dry Distillation.—Bouchardat (*Bull. Soc. Chim.* [2], xxiv. 108) has made further experiments on the distillation of caoutchouc (compare vol. i. p. 739). Five kilograms of new caoutchouc yielded 260 grams of isoprene, C^5H^8 ; 2000 grams of caoutchin, $C^{10}H^{16}$, volatile at 176° – 180° ; and 600 grams of heveene, $C^{10}H^{16}$, volatile at 266° – 265° . There remained other less volatile products, less and less fluid; some distilling below 360° , among which was probably the carbide, $C^{10}H^{14}$, and others which decomposed by heat and produced the preceding carbides. Caoutchouc may therefore be regarded as a hydrocarbon nC^5H^8 , resolvable by heat into a series of lower polymerides.

Caoutchin, washed with slightly acidulated water and rectified repeatedly from sodium, is a volatile liquid distilling at 177° – 179° . Its density is 0.865 at 0° , and 0.842 at 20° . In odour and many other properties it bears a strong resemblance to turpentine, especially in absorbing and combining with hydrochloric acid. Concentrated sulphuric acid modifies it, and produces a certain quantity of cymene, $C^{10}H^{14}$, but the larger part is converted into polymeric hydrocarbons, $C^{10}H^{12}$ and $C^{20}H^{32}$, the latter by dry distillation reproducing a terpene, $C^{10}H^{16}$. No terebene appears to be formed by the action of sulphuric acid, as the most volatile of the products does not boil below 173° (compare i. 736).

CAPILLARITY. On the Mathematical theory of Capillarity, see Roger (*Compt. rend.* lxxvi. 816); Lasowitz (*Pogg. Ann. Ergänz.* vi. 441–477).

On the Movement of Liquids in Capillary Tubes, see Decharme (*Ann. Chim. Phys.* [4], xxvii. 288; [5], i. 5–99 and 318–342; *Compt. rend.* lxxvii. 591; lxxix. 462).

On the Efflux of Liquids from Capillary Tubes, and the influence of Temperature thereon, see Guérout (*Compt. rend.* lxxviii. 351; lxxix. 1201; *Jahresb. f. Chem.* 1874, 34; *Chem. Soc. J.* 1876, i. 320); also Baumgartner (*Pogg. Ann.* cliii. 44; *Jahresb.* 1874, 35).

On the Cooling Effects produced by Capillarity: Decharme (*Compt. rend.* lxxvii. 998, 1157; *Ann. Chim. Phys.* [5], iii. 236–267; *Jahresb.* 1873, 22; 1874, 25; *Chem. Soc. J.* 1874, pp. 118, 210).

On the relations between Capillary and Electric Phenomena: Becquerel (*Compt. rend.* lxxvi. 1037; lxxix. 82; *Chem. Soc. J.* 1873, p. 1185; 1874, p. 1126); further (*Compt. rend.* lxxx. 411, 585; *Jahresb. f. Chem.* 1875, 102); also Lippmann (*Pogg. Ann.* cxlix. 546; *Phil. Mag.* [4], xlvii. 281; *Compt. rend.* lxxvi. 1407; *Chem. Soc. J.* 1873, p. 1094); further (*Ann. Chim. Phys.* [5], v. 494; *Jahresb. f. Chem.* 1875, 106).

CAPROIC ACID, $C^6H^{12}O_2$. The following table (p. 378) exhibits a comparison of the properties (1) of ordinary caproic acid, prepared from the cyanide of fermentation amyl alcohol (i. 743); (2) of normal caproic acid from normal amyl cyanide (2nd Suppl. 250); and (3) of the caproic acid contained in the crude butyric acid of fermentation (*ibid.* 251):—

From the data in this table Lieben infers that fermentation caproic acid is in all probability identical with the normal acid. He observes also that the calcium salts of all the normal fatty acids (except formic acid) contain one molecule of crystallisation-water.*

Kottal describes also the strontium salt of fermentation caproic acid, $Sr(C^6H^{11}O_2)_2 + 3H^2O$, as forming crystalline laminae having a solubility of 8.9 at 24° (in the sense of footnote, p. 378); also the cadmium salt, $Cd(C^6H^{11}O_2)_2 + 2H^2O$, having a solubility of 0.96 at 23.6° , and the zinc salt, $Zn(C^6H^{11}O_2)_2 + H^2O$, which forms indistinct crystals having a solubility of 1.03 at 24.5° .

Recent observations on the properties of normal caproic acid and its salts by Lieben a. Janacek (*Liebig's Annalen.* cxxxvii. 126; *Chem. Soc. J.* 1877, ii. 879) agree very nearly with those of Lieben a. Rossi.

For the solubility of the calcium and barium salts, Lieben a. Janacek give numbers somewhat different from those found by Kottal and by Grillone, viz., for the calcium salt, $Ca(C^6H^{11}O_2)_2 + H^2O$, 2.36 per cent. of the anhydrous salt at 12° , and for the barium salt, $Ba(C^6H^{11}O_2)_2$, 12 per cent. at 11.5° .

Normal Caproic aldehyde, $C^6H^{11}.CO.H$, prepared by the dry distillation of 10 pts. of calcium caproate and $7\frac{1}{2}$ pts. of calcium formate, forms, when pure, a limpid colourless liquid with the characteristic aldehyde odour, boiling at 127.9° under a pressure of 737.6 mm., and having a sp. gr. of 0.8498 at 0° , of 0.8335 at 20° , and of 0.8208 at 40° . With sodium bisulphite it yields a white crystalline mass. It is readily oxidised, and as readily polymerised.

* The only known exception to this law is presented by the calcium salt of fermentation butyric acid, which, according to Linnemann (*Liebig's Annalen.* cix. 196), crystallises with $2H^2O$.

	Ordinary Caproic acid	Normal Caproic acid	Fermentation Caproic acid
Free acid	Boils at 199.7° (bar. 732 mm.), slightly optically active (Lieben a. Rossi, <i>Liebig's Annalen</i> , clxv. 118).	Boils at 204.5°–205.5° (bar. 738.5 mm.) Sp. gr. = 0.9449 at 0°; 0.9294 at 20°; 0.9172 at 40°; 0.8947 at 99° (Lieben a. Rossi, <i>Gazz. chim. ital.</i> iii. 27).	Boils at 205° (bar. 746 mm.) Sp. gr. = 0.9433 at 0°; 0.928 at 20°; 0.9164 at 40°. Optically inactive (Lieben, <i>Liebig's Annalen</i> , clxx. 89).
Ethylie ether	Boils at 160.4° (corr. 2.6°) (bar. 737 mm.) Sp. gr.* = 0.887 at 0°; 0.8705 at 20°; 0.8566 at 40° (Lieben a. Rossi, <i>loc. cit.</i>)	Boils at 165.5°–166° (corr. 3.1°) (bar. 735.8 mm.) Sp. gr. = 0.8898 at 0°; 0.8732 at 20°; 0.8594 at 40° (Lieben a. Rossi, <i>loc. cit.</i>)	Boils at 166.9°–167.3° (corr. 3.5°) (bar. 738 mm.) Sp. gr. = 0.8898 at 0°; 0.8728 at 20°; 0.8596 at 40° (Lieben, <i>loc. cit.</i>)
Calcium salt	$\text{Ca}(\text{C}^6\text{H}^{11}\text{O}_2)^2 + 3\text{H}_2\text{O}$ Solubility† at 18.5° = 11.3; greater at higher temperatures.	$\text{Ca}(\text{C}^6\text{H}^{11}\text{O}_2)^2 + \text{H}_2\text{O}$ Solubility at 18.5° = 2.70; somewhat greater at the boiling heat.	$\text{Ca}(\text{C}^6\text{H}^{11}\text{O}_2)^2 + \text{H}_2\text{O}$ Solubility at 21°–22° = 4.4 (Grillone, <i>Lieb. Ann.</i> clxv. 127). Solubility at 19.5° = 2.73 (Kottal, <i>Lieb. Ann.</i> clxx. 95).
Barium salt	$\text{Ba}(\text{C}^6\text{H}^{11}\text{O}_2)^2 + 2\text{H}_2\text{O}$ Solubility at 18.5° = 34.65; less at higher temperatures (Lieben a. Rossi).	$\text{Ba}(\text{C}^6\text{H}^{11}\text{O}_2)^2$ Solubility at 18.5° = 8.49; considerably greater at higher temperatures (Lieben a. Rossi).	$\text{Ba}(\text{C}^6\text{H}^{11}\text{O}_2)^2$ Solubility at 21°–22° = 8.3 (Grillone) $\text{Ba}(\text{C}^6\text{H}^{11}\text{O}_2)^2 + 3\text{H}_2\text{O}$ Solubility at 19.5° = 2.75 (Kottal).

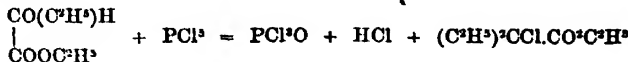
* The specific gravities are referred to water of equal temperature.

† These numbers denote the quantity of anhydrous salt contained in 100 pts. of solution saturated at the temperature specified.

Caproone or Dipentyl Ketone, $\text{CO}(\text{C}^6\text{H}^{11})^2$, found amongst the higher-boiling fractions of the crude aldehyde, is, after purification, a white crystalline body melting at 14.6° and boiling at 226.3° at a pressure of 740 mm., whilst its sp. gr. at 20° is 0.8262, and at 40° is 0.8159. Its vapour-density is 5.98.

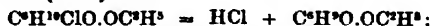
E. Schmidt found a caproone from a similar source to boil at 220°–221°, and to have a sp. gr. of 0.822 at 20° (*Chem. Soc. J.* 1872, 892). The caproone obtained by Brazier and Gossleth (i. 744) boiled at 165°, and must have been entirely dissimilar. Caproone is not acted on by sodium bisulphite solution; it forms substitution-products with bromine, and, when oxidised with bichromate, decomposes very slowly, yielding principally valeric acid and carbonic anhydride, with traces of butyric acid (Lieben a. Janacek).

Isocaproic or Diethacetic Acid, $\text{CH}(\text{C}^2\text{H}_5)_2\text{CO}_2\text{H}$. Ethylic diethoxalate (iv. 273) treated with phosphorus pentachloride, yields the ethylic ether of chlorisocaproic acid:



which by reduction with sodium-amalgam is converted into isocaproic acid.

Chlorisocaproic ether is resolved by distillation into hydrochloric acid and ethyl-crotonic ether, $\text{C}^2\text{H}_5(\text{C}^2\text{H}_5)\text{O.CO}^2\text{C}^2\text{H}_5$:



and the ethyl-crotonic ether, treated with sodium-amalgam, takes up 2 at. hydrogen and is converted into isocaproic ether, $\text{C}^2\text{H}_5\text{O.CO}^2\text{C}^2\text{H}_5$, which by saponification yields isocaproic acid. Both processes yield at the same time ethyl-crotonic acid, which boils at nearly the same temperature as isocaproic acid, and is therefore difficult to separate.

Ethyl-crotonic acid unites with *bromine*, forming dibromisocaproic acid, $C^2H^{10}Br_2O^2$, which is crystalline and melts at 177° (Drobasgill, *Deut. Chem. Ges. Ber.* vi. 1175).

Ethodimethacetic Acid, $\begin{matrix} H^1C \\ H^2C \end{matrix} \{ C(C^2H^3).CO^2H$. This is another isomeride of caproic acid, the nitril of which is formed by the action of potassio-mercuric cyanide, $2KCy.HgCy^2$, on ethyl-dimethyl-carbinyl cyanide, $(CH^3)^2C(C^2H^3).CN$. The crude product of the reaction boils between 130° and 190° , and yields, by repeated fractional distillation, a portion which boils at 130° and solidifies in a mixture of ice and salt; and this, which is the pure nitril, is converted, by heating with fuming hydrochloric acid, into ethodimethacetic acid, which boils at 187° , and crystallises at -14° . Its *barium salt*, $(C^2H^{11}O^2)^2Ba + 5H^2O$, crystallises in large scales (Wishnegradskey, *Deut. Chem. Ges. Ber.* vii. 730).

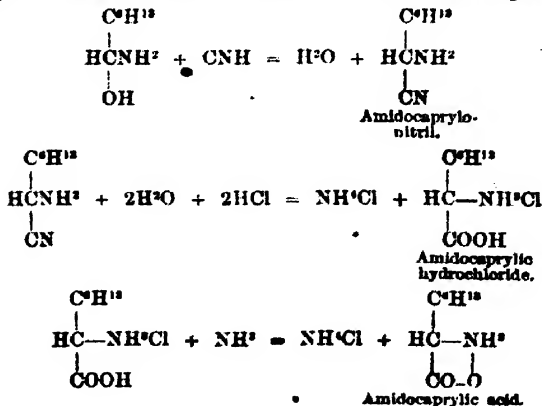
CAPRYLIC ACID, $C^8H^{16}O^2$. The identity, first pointed out by Zincke (1st *Suppl.* 395) of the 8-carbon fatty acids prepared: (1) by saponification of coconut oil, and (2) by oxidation of octyl alcohol from Heracleum oil (octylic acid), has been confirmed by the experiments of J. van Rönse (Liebig's *Annalen*, clxxi. 380), who gives the following comparison of the properties of the acids from those two sources and of some of their salts:—

	Octylic acid	Caprylic acid
$C^8H^{16}O^2$	Boils between 235° and 238° , under 757.8 mm. pressure; melts at 16° to 17° .	Boils between 236° and 237° , under 761.7 mm. pressure; melts at 16° to 16.5° .
$C^2H^3.C^6H^{13}O^2$	Boils between 207° and 208° , under 763.2 mm. pressure. Sp. gr. at $0^\circ = 0.8866$; at $16^\circ = 0.8732$.	Boils between 207° and 208° , under 763.1 mm. pressure. Sp. gr. at $0^\circ = 0.8871$; at $16^\circ = 0.8730$.
$Ba(C^6H^{13}O^2)^2$	Crystallises in small anhydrous plates; 100 parts of water dissolve 0.6101 of salt at 20° .	Crystallises in small anhydrous plates; 100 parts of water dissolve 0.6204 of salt at 20° .
$Ca(C^6H^{13}O^2)^2.H^2O$	Water lost at 130° .	Water lost at 130° .
$Zn(C^6H^{13}O^2)^2$	Fine anhydrous crystals, melting at 136° .	Fine anhydrous plates, melting between 135° and 136° .

As the octyl alcohol of Heracleum oil is the isoprimary alcohol (2nd *Suppl.* 868), the caprylic acid formed from it must have the constitution $(CH^3)^2-(CH^2)^4-COOH$.

Derivatives of Caprylic Acid.

Amidocaprylic Acid, $C^8H^{15}NO^2 = C^8H^{15}(NH^2)O^2$ (Erlenmeyer & Sigel, *Liebig's Annalen*, clxxvi. 341). This acid is formed by treating normal heptaldehyde-ammonia, $C^7H^{15}O.NH^2$ or $C^7H^{14}(NH^2).OH$ (ænanthol-ammonia) with hydrocyanic acid, boiling the resulting cyanide, $C^8H^{14}(NH^2).CN$, with hydrochloric acid, and decomposing the chlorinated acid (amidocaprylic hydrochloride) thereby produced with ammonia. The successive steps of the reaction may be indicated by the following equations:



The amido-acids (glycocines) of the fatty series, to which amidocaprylic acid belongs, are usually represented by the general formula $C^aH^{2a+1}-CH(NH^2)-COOH$; but this formula does not easily account for their property of uniting with acids as well as with bases. Hence Erlenmeyer and Sigel propose to represent them by the general formula $C^aH^{2a+1}-CH-NH^2$, of which that above given for amidocaprylic acid is an example.

This formula easily explains the combination of the molecule with an acid, HCl for example, by the attachment of Cl to the group NH^2 , of H to COO, and the severing of the link between O and N. The formula thus altered represents an ordinary acid containing the carboxyl group, viz. $C^aH^{2a+1}-CH-NH^2Cl$

Amidocaprylic acid crystallises in white laminae having a mother-of-pearl lustre, very slightly soluble in alcohol, ether, and cold water, soluble in 150-160 parts of hot water. The solution is perfectly neutral to vegetable colours. The acid, when carefully heated on platinum foil, volatilises completely without previous fusion.

Salts of Amidocaprylic acid.—The *hydrochloride*, $C^aH^{2a+1}-CH-NH^2Cl$, separates on cooling from a solution of amidocaprylic acid in hot dilute hydrochloric acid, in broad needles, but on evaporation of a solution prepared in the cold over sulphuric acid, in asbestos-like needles. In both cases the crystals have a silky lustre, which they retain in dry air; in moist air they become dull, and give off hydrochloric acid.

Amidocaprylic Nitrate, $C^aH^{2a+1}-CH-NH^2NO^2$, prepared by cooling a warm solution of amidocaprylic acid in nitric acid, forms slender needles. By slow evaporation of a cold solution over sulphuric acid, large well-formed crystals of the triclinic system are obtained. The nitrate contains no water of crystallisation, and keeps its brilliancy in dry air.

Amidocaprylic Sulphate, $(C^aH^{2a+1}NO^2)^2.SO^2H^2$, separates out on evaporating a solution of amidocaprylic acid in dilute sulphuric acid in a desiccator, in the form of four-sided tables, which cannot easily be freed from adhering sulphuric acid, since the salt is very readily decomposed by water.

Cupric Amidocaprylate, $(C^aH^{2a+1}NO^2)^2Cu = C^aH^{2a+1}-CH-NH^2Cu$, is obtained by mixing a boiling solution of the acid with cupric chloride.

Amidocaprylonitril, $C^aH^{2a+1}N^2 = C^aH^{2a+1}-CH-NH^2CN$, is formed, together with imidocaprylonitril, $C^aH^{2a+1}N^2$, by the action of hydrocyanic acid on œnanthol-ammonia. To prepare it, 90 grams of œnanthol-ammonia and 120 grams of hydrocyanic acid (20 per cent.) are shaken up in a well-stoppered vessel till the temperature ceases to rise, whereupon the liquid separates into two layers. After pouring off the aqueous layer, about 150 grams of hydrochloric acid (5 per cent.) are added, and after shaking the liquid and leaving it to clarify, the hydrochloric acid solution is poured off from the oily layer, and the latter is again treated with about 100 grams of acid. The undissolved oil is the pure imidonitril. The acid solution also still contains some of this nitril, which is extracted by ether. The solution is next exactly neutralised with ammonia, when the amidonitril separates as a yellowish oil. This oil is dissolved in ether; the solution is dehydrated by calcium chloride; hydrochloric acid gas is passed into the anhydrous liquid; and the crystalline precipitate obtained is filtered off and washed with absolute ether. When repurified by solution in alcohol and precipitation with absolute ether, the *hydrochloride of amidocaprylonitril* is obtained in crystals, from which, when exactly neutralised with ammonia, the pure amidonitril separates. This nitril is an almost colourless oil, which has a peculiar somewhat sharp smell, and solidifies at -5° to -6° , but liquefies afterwards at 0° . It is miscible in all proportions with alcohol and ether, but is almost insoluble in water. It dissolves perfectly in very dilute hydrochloric acid, but loses this property on keeping, because it becomes changed, with loss of ammonia, into the imidonitril.

The *hydrochloride*, $C^aH^{2a+1}N^2.HCl = C^aH^{2a+1}-CH-NH^2Cl$, crystallises in white satiny, six-sided plates, easily soluble in water and in alcohol, insoluble in absolute ether, very slightly soluble in strong hydrochloric acid. The *platinochloride*, $2(C^aH^{2a+1}N^2.HCl).PtCl_4$, separates on adding platinum chloride to a solution of the hydrochloride, in shining yellow plates, nearly insoluble in water, easily soluble in alcohol and in a mixture of alcohol and ether, insoluble in absolute ether.

The hydrochloride, boiled with hydrochloric acid (sp. gr. 1.10), is completely converted into amidocaprylic hydrochloride. When hydrochloric acid gas is passed to saturation into an aqueous solution of amidocaprylonitril hydrochloride, with constant cooling, almost the whole of the dissolved salt separates without change in the crystalline form; but if the vessel is dipped only from time to time into cold water, a precipitate is formed consisting of a mixture of the hydrochlorides of amidocaprylonitril and amidocaprylamide. If the hydrochloric acid gas is passed into the liquid without cooling, great heat is evolved, and the separation of crystals does not take place till the liquid has attained its highest temperature.

Amidocaprylamide, $C^8H^{12}N^2O = C^8H^{11}(NH)COONH^2$. To separate this base, the hydrochloride, obtained as just described, is freed from the mother-liquor and recrystallised from boiling alcohol. A cold saturated solution of the salt is then mixed with ammonia and shaken up with ether. After evaporation of the ether, a colourless syrup is left, which has a strong alkaline reaction, and gradually crystallises. The base is so difficult to prepare free from carbonate that its properties in the free state have not been examined.

The **hydrochloride**, $C^8H^{12}N^2O.HCl$, prepared as above, crystallises in small, brilliant, flat prisms, which are more soluble in water and alcohol when hot than when cold. It is precipitated from its solution by hydrochloric acid. The **platinochloride**, $2(C^8H^{12}N^2O.HCl).PtCl^4$, is precipitated from a solution of the hydrochloride on addition of a neutral solution of platinum chloride, in four-sided plates with truncated summits, which dissolve sparingly in water but are more easily soluble in alcohol.

Carbonate of Amidocaprylamide.—Attempts were made to prepare this salt (1) by passing carbon dioxide into an aqueous solution of the free base; (2) by mixing a saturated solution of hydrochloride of amidocaprylamide with sodium bicarbonate; (3) by mixing the solution with sodium monocarbonate. The results obtained in these reactions gave, as the approximate formula of the body $(C^8H^{12}N^2O)^2CO^2$. The salt obtained is therefore not a regular carbonate of the amido-amide, since it wants a molecule of water, the elements of which must have been separated during its formation.

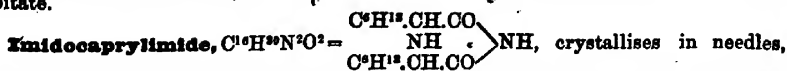
When this salt is mixed with a solution of barium chloride at ordinary temperature, hard, warty, crystalline bodies separate after a time, and stick to the sides of the vessel. If the solutions are heated on the water-bath, or boiled, pure barium carbonate is thrown down. The crystalline precipitate appears to be the barium salt of **caprylamidimidocarbonic acid**, $C^8H^{12}N^2O^2$, or $C^8H^{12}...CH^2 \begin{smallmatrix} \diagup CONH^2 \\ \diagdown NH \end{smallmatrix} ...CO^2H$, which is produced simultaneously with the hydrochloride of amidocaprylamide. The compound formed by the action of carbon dioxide or sodium carbonate on amidocaprylamide, is the amidocaprylamide salt of this acid, $C^8H^{12}N^2O^2 + (C^8H^{12}N^2O = C^8H^{12}N^2O^2)$. On heating this salt with caustic potash on the water-bath, it splits up into potassium carbonate, ammonia, and amidocaprylic acid. In like manner, the hydrochloride of amidocaprylamide, heated with hydrochloric acid, splits up into the hydrochloride of amidocaprylic acid and sal-ammoniac, so that a progressive change takes place from the amidonitril through the amide into the amido-acid.

Imidocaprylonitril, $C^8H^{12}N^2 = \begin{smallmatrix} C^8H^{12} \\ \diagup CN \end{smallmatrix} CH-NH-CH \begin{smallmatrix} \diagdown CN \end{smallmatrix} C^8H^{12}$. When the product of the action of hydrocyanic acid on α -naphthol-ammonia (p. 570) is treated with dilute hydrochloric acid, amidocaprylonitril is dissolved, and imidocaprylonitril remains in the form of a thick colourless oil, which crystallises between 5° and 6° , dissolves easily in alcohol and ether, very sparingly in water and in dilute hydrochloric acid. It is decomposed by boiling with silver nitrate, yielding silver cyanide and α -naphthol. On heating it for half an hour with 15 parts of hydrochloric acid in a vessel with vertical condenser, and then distilling, formic acid, hydrocyanic acid, and α -naphthol pass over, while amidocaprylic acid remains behind. With fuming hydrochloric acid at 105° it yields the same products, with the exception of hydrocyanic acid. With the same acid at the temperature of the water-bath, the products are **imidocaprylic acid** and **imidocaprylimide**, separable by boiling with sodium carbonate, which dissolves only the former.

Imidocaprylic acid, $C^8H^{12}NO^2 = \begin{smallmatrix} C^8H^{12} \\ \diagup CN \end{smallmatrix} CH^2CO.OH$, is a white tasteless powder, $C^8H^{12}CH.CO.OH$

which becomes pasty at 180° , brown at 180° – 190° , and melts with decomposition between 210° and 215° . When boiled with hydrochloric acid of the strength of 20 per cent. it dissolves without decomposition, and the solution on cooling deposits brilliant needle-shaped crystals of the hydrochloride of imidocaprylic acid; but when heated to 180° with hydrochloric acid of 40 per cent. it is resolved into amidocaprylic

acid and polymerised cyanthol. *Calcium imidocaprylate* is a cryptocrystalline precipitate.



melts at 79.5° , is insoluble in cold and nearly insoluble in hot water. Hot strong potash-ley converts it into imidocaprylic acid. Its hydrochloride crystallises in needles, and is decomposed by boiling water.

CARBACETOXYLIC ACID, $C^3H^4O^4$. On the formation of this acid from β -chloropropionic acid, see **PROPIONIC ACID**.

CARBALLYLIC ACID. See **TRICARBALLYLIC ACID**.

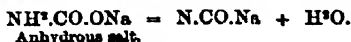
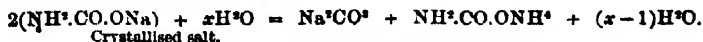
CARBAMIC ACID, $NH^2.CO.OH$. This acid is formed, together with carbonic, oxalic, and oxamic acids, and water, by oxidising glycocine in ammoniacal solution with potassium permanganate. The carbamic acid is a direct product of the oxidation, and its ammonium-derivative appears to be formed whenever carbon dioxide and ammonia come together in the nascent state, and therefore in the animal organism. Ammonium carbamate has in fact been found in the serum of dogs' blood, and this salt is convertible by dehydration into urea, which is the amide of carbamic acid. Ammonium carbamate is also produced by the oxidation of ammoniacal solutions of sodium formate, leucine, tyrosine, and albumin with ammonium permanganate (Drechsel, *J. pr. Chem.* [2], xii. 417).

Carbamates. The only carbamates hitherto known are the ammonium salt and the alcoholic carbamates or urethanes; but Drechsel (*J. pr. Chem.* [2], xvi. 180) has lately prepared and examined the carbamates of the fixed alkalis and alkaline earths.

Ammonium Carbamate, $NH^2.CO.ONH^4$.—When carbon dioxide is passed into milk of lime diluted with 3–4 times its volume of strong aqueous ammonia, a clear liquid is obtained, which is decomposed by heat, with separation of calcium carbonate, and by sodium carbonate, with immediate precipitation of the same salt. It appears then that carbamic acid is formed by the union of carbon dioxide and ammonia gases in presence of water, showing that the affinity between these gases is greater than that between lime and carbon dioxide, and affording strong grounds for regarding aqueous ammonia as simply a solution of the gas in water. Ammonium carbamate in solution is slowly converted into the carbonate. The conversion is, however, incomplete, and is much impeded by the presence of free ammonia. Even on long boiling of its solution, the carbamate is not completely decomposed, and in presence of ammonia it is comparatively stable. Conversely, ammonium carbonate, in aqueous solution, parts with the elements of water and is converted into the carbamate.

Sodium Carbamate, $NH^2.CO.ONa$, is prepared by gradually adding an alcoholic solution of sodium ethylate to a solution of ammonium carbamate in aqueous ammonia, the liquid, according to its concentration and temperature, yielding either crystals, or an oil which, on addition of absolute alcohol, solidifies to a crystalline mass. The crystals thus obtained are fine prisms containing water of crystallisation, and very efflorescent. If placed in a closed vessel while still retaining their water of crystallisation, they soon decompose, with evolution of ammonia. Placed over sulphuric acid, they quickly lose their water at ordinary temperatures, and the dry salt may then be kept without alteration.

Sodium carbamate is very soluble in water. The recently prepared solution made with anhydrous salt even several days old, remains quite clear on being mixed with solution of calcium chloride, and only gradually becomes turbid, just like a solution of pure calcium carbamate. The salt when heated decomposes in different ways, accordingly as it is anhydrous or crystallised. In the latter case it gives off large quantities of ammonia, water, and carbon dioxide (or ammonium carbonate), and the residue, which does not melt at a gentle heat, contains nothing but sodium carbonate; the anhydrous salt, on the other hand, gives off less ammonia, and leaves a partially fusible residue containing sodium cyanate. These decompositions may be represented by the following equations:—



The water produced in the latter case acts on another portion of the dry salt in the manner shown by the first equation.

Potassium Carbamate, $\text{NH}^2\text{CO.OK}$, is prepared, (1) By adding a solution of potassium in absolute alcohol to the ammoniacal, mother-liquor remaining from the preparation of ammonium carbamate. The liquid after a few hours, or more quickly at 0° , yields small needles and prisms of the anhydrous salt. (2) By saturating a solution of potassium in absolute alcohol with ammonia gas at 0° , and passing dry carbon dioxide into the liquid, whereby an amorphous flocculent precipitate is formed, which, after standing in the mother-liquor for some hours, changes into a crystalline mass of granules and small needles.

This salt, when heated, decomposes exactly in the same manner as the anhydrous sodium salt, the residue fusing partially and containing potassium cyanate, which, as in the case of the sodium salt, is decomposed by the water separated in the first instance. No cyanamide is formed by the decomposition of either of these salts.

Calcium Carbamate, $(\text{NH}^2\text{CO.O})^2\text{Ca}$, is prepared by passing carbon dioxide into strong aqueous ammonia (sp. gr. 0.945 or lower), and gradually adding fresh milk of lime till it no longer dissolves even on brisk agitation—the liquid, on the other hand, beginning to deposit crystals. These are left for a while to separate, and the solution is then poured into about an equal volume of absolute alcohol cooled to 0° , whereupon a thick amorphous precipitate is formed which becomes crystalline after a while. It is then introduced into a wide glass tube containing a filter of glass-wool and well-washed sand; the mother-liquor is drawn off; and the precipitate is once washed with a mixture of absolute alcohol and strong ammonia in about equal volumes, then with absolute alcohol, lastly with absolute ether, and immediately dried by quickly drawing a current of dry air through the tube. The rapid evaporation of the dry ether causes a reduction of temperature sufficient to prevent decomposition of the salt.

Calcium carbamate thus prepared is a very fine crystalline powder made up of microscopic prisms, which have the composition $2(\text{NH}^2\text{CO})^2\text{Ca} + \text{H}^2\text{O}$, and exhibit forms often assumed by gypsum. It dissolves in water, forming a solution which is perfectly clear at first, but soon becomes turbid from separation of calcium carbonate. The addition of ammonia renders the solution more stable, the stability being greater as the ammonia is stronger. From a saturated solution in warm ammonia the salt crystallises on cooling to 0° in splendid four-sided prisms 1–2 mm. long. When recently prepared it is scentless, but even after a few hours it begins to smell of ammonia, being decomposed by its own water of crystallisation. Acids, even acetic acid, decompose it with effervescence. The crystallised salt, heated to 95° – 100° , gives off ammonia and aqueous vapour (? carbon dioxide), and leaves a residue apparently consisting of carbamate and carbonate of calcium:



The anhydrous salt is stable at 180° , and decomposes only at the softening point of ordinary glass, being resolved into CO^2 , water, and calcium cyanide, i.e. cyanamide CN^2H , having its two hydrogen atoms replaced by Ca:



Strontium Carbamate, $(\text{NH}^2\text{CO.O})^2\text{Sr}$, prepared like the calcium salt, crystallises in white, shining, anhydrous laminae, forming with water a solution which is perfectly clear when first prepared, but almost instantly becomes turbid. The ammoniacal solution, on the other hand, is permanent, or deposits carbonate after some time only. The crystallised salt being anhydrous keeps much better than the calcium salt. When heated it decomposes like the anhydrous calcium salt, yielding a small quantity of crystalline sublimate, and leaving a residue of strontium cyanide.

Barium Carbamate appears to be formed by passing carbon dioxide into aqueous ammonia and adding baryta-water, but it cannot be obtained in the solid state, as it rapidly decomposes with formation of barium carbonate. A double salt of carbamate and chloride of barium, $(\text{NH}^2\text{CO.O})^2\text{Ba.BaCl}^2$, may however be prepared by passing carbon dioxide into a solution of barium chloride mixed with strong ammonia, till crystals begin to form, then filtering, mixing the filtrate with $\frac{1}{2}$ – $\frac{3}{4}$ vol. alcohol, and immersing the containing vessel in ice-cold water. The double salt then separates as a granular crystalline powder, which may be washed in the manner above described and dried. Its solution in water is clear at first, but very quickly becomes cloudy; the ammoniacal solution is somewhat more stable.

The mode of decomposition by heat of the carbamates of the alkaline earth-metals appears at first sight to be different from that of the carbamates of the alkali-metals, inasmuch as a cyanide, or metallic derivative of cyanamide, is produced in the former case, and a cyanate in the latter. This difference is, however, only apparent, since the cyanates of the alkaline earth-metals, which may be supposed to be formed in the

first instance, are resolved, on further heating, into carbon dioxide and cyanides, e.g. $(\text{CON}^2\text{Ca} = \text{CO}^2 + \text{CN}^2\text{Ca}$ (see CYANAMIDE).

All the metallic carbamates yet examined behave therefore in the same manner when heated, being resolved into water and metallic cyanates :

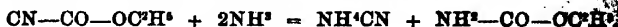


Ammonium carbamate also decomposes in the same manner, but the resulting cyanate of ammonium is not resolved into a cyanide and carbon dioxide, like the carbamates of the alkaline earth-metals, but directly converted into carbamide (urea) $\text{CO}(\text{NH}^2)^2$.

The change which takes place in this decomposition of the carbamates, viz., separation of water, is exactly the same as that which occurs in the formation of nitrils from amides: hence the cyanates formed in this reaction are normal cyanates, like cyanetholine and its homologues, which are produced by the action of cyanogen chloride on the sodium-alcohol, (1st Suppl. 519).

Alcoholic Carbamates.—Urethanes.

Ethyl Carbamate, or Urethane, is formed, together with ammonium cyanide, by the action of alcoholic ammonia on ethyl cyanocarbonate:



Phenyl-urethane, $\text{NH}^2\text{—CO—OC}^6\text{H}^5$, is formed in like manner, together with hydrogen cyanide, by the action of aniline on ethylic cyanocarbonate (Weddige, *J. pr. Chem.* [2], vii. 79).

Acetyl-ethyl-Carbamate, $\text{C}^2\text{H}^3\text{NO}^2 = \text{NH}(\text{C}^2\text{H}^3\text{O})\text{—CO—OC}^2\text{H}^5$, is formed by heating urethane with acetyl chloride to 110° . It crystallises in slender needles, dissolves in ether-alcohol; melts at $77^\circ\text{—}78^\circ$ (Kretzschmar & Salomon, *J. pr. Chem.* [2], x. 28).

Aldehydic Urethanes (C. Bischoff, *Deut. Chem. Ges. Ber.* vii. 628, 1078). These bodies, related to the chlorinated compound $\text{C}^2\text{H}^3\text{Cl}^2\text{N}^2\text{O}^2$, which Stenhouse obtained by the action of chlorine on an alcoholic solution of mercuric cyanide (ii. 218; 2nd Suppl. 410), are produced by the action of aldehydes and of acetal on urethanes in presence of strong condensing agents, chiefly hydrochloric acid.

Ethidene-urethane, $\text{C}^4\text{H}^{10}\text{N}^2\text{O}^2 = \text{CH}^2\text{CH}(\text{NH.CO.OC}^2\text{H}^5)^2$, of which Stenhouse's compound is the dichloro-derivative, is formed by adding hydrochloric acid to a solution of urethane in acetal, the mixture solidifying after some time to a crystalline pulp of very fine needles melting at 125° (Bischoff). The same compound separates after a while from a solution of urethane in acetaldehyde, and immediately, with great rise of temperature, on adding to the solution a few drops of hydrochloric acid. From the cooled solution it is precipitated by water in needles having a satiny lustre; melting at 126° ; tasteless and scentless; easily soluble in ether, alcohol, and hot water, less easily in cold water; decomposing when distilled (Nencki, *Deut. Chem. Ges. Ber.* vii. 158).

Chlorethidene-urethane, $\text{C}^4\text{H}^{10}\text{ClN}^2\text{O}^2 = \text{CH}^2\text{Cl—CH}(\text{NH.CO.OC}^2\text{H}^5)^2$, is formed by the action of chlorine on a strong solution of hydrocyanic acid in alcohol (2nd Suppl. 410); also on adding a somewhat considerable quantity of very strong hydrochloric acid to a solution of urethane in monochloroacetal. On dissolving the crude crystalline pulp thus obtained in alcohol, and mixing the solution with hot water, the liquid first deposits the excess of chloroacetal in oily drops, and the milky liquid separated therefrom gradually yields crystals of pure chlorethidene-urethane melting at 147° (Bischoff).

Chloral-urethane, $\text{C}^3\text{H}^5\text{ClN}^2\text{O}^2 = \text{CCl}^3\text{—CH}(\text{NH—CO—OC}^2\text{H}^5)^2$.—A solution of urethane in chloral, mixed with strong hydrochloric acid, gradually solidifies to a mass which may be purified by washing with water. If sulphuric acid be used instead of hydrochloric acid, the mixture becomes glutinous, and on addition of water remains at the bottom of the vessel as an oily mass, which gradually becomes crystalline. The solid product obtained in either case separates from ether-alcohol as a laminar crystalline mass, having the composition above given. The same compound is formed on adding urethane to fused chloral hydrate, and treating the mixture with hydrochloric or sulphuric acid.

Chloral-urethane is insoluble in cold water, and is resolved by hot water into chloral and urethane; it dissolves easily in alcohol and in ether. It has a faint odour of chloral, melts at 103° , and is easily resolved at a higher temperature into components. With potash it yields the decomposition-products of chloral.

Bromal-urethane is very much like the preceding compound, and melts at 132°.

Butylchloral-urethane, $C^4H^9Cl^1NO^2 = C^4H^8Cl^1-CH \begin{smallmatrix} OH \\ NH-CO^2C^4H^8- \end{smallmatrix}$ On adding urethane to a mixture of butyl-chloral, $C^4H^8Cl^1.CHO$, and strong hydrochloric acid, this compound separates after some time in white, very hard, brittle prisms, yielding by analysis 40.3 per cent. chlorine and 5.4 nitrogen, the formula requiring 40.3 chlorine and 5.3 nitrogen.* It melts at 123°-125°, and when heated with lime gives off an odour like that of collidine. In all other respects it resembles chloral- and bromal-urethane.

Valeral-urethane, $C^5H^{11}N^2O^2 = C^5H^9-CH(NH.CO.OCC^5H^9)^2$, homologous with ethidene-urethane, is formed on adding a small quantity of strong hydrochloric acid to a solution of urethane and valeral, the liquid immediately becoming hot and concreting to a solid mass. It is perfectly inodorous when dry; smells faintly of valeral when moist; dissolves easily in warm alcohol, and separates therefrom on addition of hot water in long silky needles; melts at 126°; sublimes with partial decomposition; and when more strongly heated yields an oily distillate having an aromatic odour. When heated with dilute acids it is easily resolved into urethane and valeral.

Chlorovaleral-urethane, $C^5H^9Cl-CH(NH.CO.OCC^5H^9)^2$, is formed on adding hydrochloric acid to a mixture of chlorovaleral and urethane. It melts at 130°, and is more soluble than valeral-urethane. In preparing this compound it is best to operate with the smallest quantities, since an excess of chlorovaleral adheres obstinately to the product.

Benzal-urethane, $C^7H^7-CH(NH.CO.OCC^7H^7)^2$, is formed by adding a small quantity of strong hydrochloric acid to a solution of urethane in bitter almond oil (in theoretical quantity, or with a slight excess of urethane), the liquid immediately solidifying, with considerable rise of temperature and disappearance of the odour of bitter almond oil. This compound dissolves sparingly in cold, very easily in hot alcohol, and crystallises very finely from the solution on addition of boiling water. It forms a white, perfectly inodorous, crystalline mass, having a silky lustre, melts at 171°, sublimes undecomposed when cautiously heated, but immediately gives off the odour of bitter almond oil when heated with dilute acids.

Cinnamal-urethane, $C^9H^9(NH.CO.OCC^9H^9)^2$, is formed on adding hydrochloric acid in small quantity (a larger quantity decomposes the product) to a solution of urethane in commercial oil of cassia: The crude product must be washed first with water, then with ether. The compound is nearly insoluble in ether, dissolves easily but with partial decomposition in warm alcohol. It is completely decomposed by boiling with water, still more readily with dilute acids. It has no constant melting point, but softens gradually when heated, and melts completely between 135° and 143°.

Cuminal-urethane is very much like the preceding compound, and crystallises in needles from its alcoholic solution after dilution with hot water.

Anisal-urethane, $C^8H^7 \begin{smallmatrix} OCH^3 \\ CH(NH.CO.OCC^8H^7)^2 \end{smallmatrix}$ formed from anisaldehyde and urethane, crystallises from a mixture of equal quantities of boiling alcohol and water, in splendid long needles having a silky lustre, and melting at 171°-172°; it dissolves sparingly in cold, easily in hot alcohol.

A mixture of salicylic aldehyde and urethane, treated either with hydrochloric or sulphuric acid, did not yield any product fit for analysis.

Furfural-urethane, $C^5H^4O-CH(NH.CO.OCC^5H^4O)^2$, separates immediately on adding a drop of strong hydrochloric acid to a mixture of furfural and urethane, and stirring. The reaction is very violent, and must be moderated by cooling. The compound is insoluble in water, but dissolves easily in alcohol and ether, and crystallises from dilute alcoholic solutions, in splendid silky needles resembling sulphate of quinine. It melts at 169°.

Propyl Carbamate or Propyl-urethane, $C^3H^7NO^2 = NH^2.CO.OCC^3H^7$, is prepared by digesting urea with excess of propyl alcohol: $CH^3N^2O + C^3H^7O = NH^2 + C^3H^7NO^2$. On dissolving the product in ether, expelling the ether and excess of propyl alcohol by evaporation, and digesting the residue with water, propyl allophanate remains undissolved, and the filtrate when evaporated leaves propyl-urethane, in long, shining, transparent prisms, easily soluble in water, alcohol, and ether, melting at 50°-52°, boiling at 194°-196°. In the moist state it is decomposed by heat, with evolution of ammonia (Cahours, *Compt. rend.* lxxvi. 1387).

off's paper this compound is regarded as crotonchloral-urethane, $C^3H^5Cl^1NO^2 = NH-CH=CH-CHCl^1-CH^2-CH^3$, which requires 40.6 Cl and 5.2 N; but as Pinner has shown that a croton chloral is really butyl chloral (p. 50), there can be no doubt that the compound under consideration is butylchloral-urethane, the formula of which indeed agrees with the percentage of chlorine more closely than that of crotonchloral-urethane.

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Ethidene-propyl-urethane, $\text{CH}^3\text{—CH}(\text{NH}\cdot\text{CO}\cdot\text{O}\cdot\text{C}^3\text{H}_7)^2$, is formed, though less easily than the corresponding ethyl-compound, on adding strong hydrochloric acid to a solution of propyl-urethane in acetaldehyde. It is easily soluble in alcohol, and crystallises from weak spirit in fine white needles melting at $115^\circ\text{—}116^\circ$.

Valeral-propyl-urethane crystallises in fine white needles.

Benzal-propyl-urethane, formed from bitter almond oil, propyl-urethane, and hydrochloric acid, is precipitated by hot water from its solution in boiling alcohol as a white crystalline powder melting at 143° .

Succinyl-carbamic Acid, $\text{C}^4\text{H}^3\text{N}^2\text{O}^4 = \begin{array}{l} \text{CH}^3\text{—COOH} \\ | \\ \text{CH}^3\text{—CONH—CO—NH}^2 \end{array}$, is produced by heating urea with an equivalent quantity of succinic anhydride to $120^\circ\text{—}130^\circ$:



The two compounds melt together to an oily liquid which solidifies suddenly after a few minutes. After washing with alcohol to remove unaltered succinic anhydride, and once recrystallising from water, the succinyl-carbamic acid is obtained quite pure. It crystallises in small shining scales, nearly insoluble in cold water, alcohol, and ether, moderately soluble in glacial acetic acid and in hot water. Strong sulphuric acid dissolves it in all proportions; but on addition of water, the succinyl-carbamic acid is immediately precipitated in its original state. This acid forms soluble salts with ammonia and the fixed alkalis, insoluble salts with mercury, silver, and other heavy metals. The crystals, when slowly heated, melt with complete decomposition at 195° ; when quickly heated they melt at $203^\circ\text{—}205^\circ$ (W. H. Fike, *Deut. Chem. Ges. Ber.* vi. 1312).

Thiocarbamic Acid, $\text{NH}^2\cdot\text{CS}\cdot\text{SH}$. This compound has been already described (v. 490) as *sulphocarbamic acid*.

Thiocarbamic Sulphide or Sulphanhydride, $(\text{NH}^2\cdot\text{CS})^2\text{S}$,—also called *Hydrothioprussic acid* (Gmelin's *Handbook*, Eng. ed. viii. 98)—and a number of its derivatives were described by Zeise in 1842 (*Liebig's Annalen*, xlviii. 95).

The *ammonium-salt*, $[\text{NH}(\text{NH}^4)\cdot\text{CS}]^2\text{S}$, obtained by the action of carbon disulphide on alcohol saturated with ammonia gas, or by treating ammonium thiocarbonate with alcohol, forms large shining crystals of lemon-yellow or orange-yellow colour, neutral to vegetable colours, inodorous when recently prepared, but smelling of hydrogen sulphide after exposure to the air; decomposing at 160° , with formation of hydrogen sulphide, carbon sulphide, ammonium thiocarbonate, and a white needle-shaped salt apparently consisting of ammonium cyanide.

When the solution of this salt in 3 parts of water is mixed with sulphuric or hydrochloric acid diluted with twice its quantity of water, and a larger quantity of water then added, the thiocarbamic sulphide, $\text{C}^2\text{N}^2\text{H}^4\text{S}^2$, separates as a transparent colourless oil which remains permanent for a short time under the acid liquid, but decomposes during the attempt to separate it therefrom.

The solution of the ammonium salt gives with cupric salts a yellow flocculent precipitate of the *copper compound*, $\text{Cu}(\text{NH}\cdot\text{CS})^2\text{S}$, which, after washing with water, does not change, by keeping, but is resolved by boiling with water into thiocyanic acid and cupric sulphide. The *lead* and *mercuric* salts are white precipitates which quickly decompose into thiocyanic acid and metallic sulphides. The *sine salt* is more permanent, and is obtained as a white precipitate, in which olive-green pyramidal crystals, apparently consisting of the same salt, form in a few days (Zeise).

The *phenyl-ammonium salt*, $\text{C}^6\text{H}^5\text{N}^2\text{S}^2 = [\text{NH}^2(\text{C}^6\text{H}^5)\text{—NH—CS}]^2\text{S}$, is prepared by mixing aniline with carbon disulphide and ammonia. Prismatic crystals then begin to separate, and in a few minutes the whole solidifies to a crystalline pulp. This salt is also rather unstable, and is best purified by washing with ether, after the mother-liquor has been squeezed out. It dissolves readily in boiling alcohol, and crystallises therefrom in fine dense glassy prisms, mixed however with laminar crystals of thiocarbaniide, $\text{C}^6\text{H}^5\text{N}^2\text{S}$, into which, moreover, the phenyl-ammonium salt is quickly and completely converted by boiling with water. This reaction affords a very convenient method of preparing thiocarbaniide (Hlasiwetz & Kachler, *Liebig's Annalen*, clxvi. 142).

Thiocarbamic Disulphide, $(\text{NH}^2\cdot\text{CS})^2\text{S}^2$, is the compound, usually called *hydranthion*, obtained by the action of chlorine-water on ammonium thiocarbonate (iii. 179).

Thiocarbamic acid and its derivatives just described, may be supposed to contain the radicle NH^2CS , designated by Hlasiwetz & Kachler as thiuram: thus— $\text{NH}^2\text{CS.SH}$. Thiuram sulphhydrate (Thiocarbamic acid).
 $(\text{NH}^2\text{CS})_2\text{S}$. Thiuram sulphide.
 $[\text{NH}(\text{NH}^2)\text{CS}]_2\text{S}$. Ammonium-thiuram sulphide, &c.

Action of Ammonium Thiocarbamate on Aldehydes.—The product obtained with acetaldehyde is carbothialdine, $\text{C}^2\text{H}^4\text{N}^2\text{S}^2$ (i. 802), which is regarded by E. Mulder (*Liebig's Annalen*, clixviii. 228) as thiocarbamate of diethylidene-ammonia, $\text{NH}^2\text{CS}\cdot\text{N}(\text{CH}_2\text{CH}^3)_2$, and by Hlasiwetz (*loc. cit.*) as thiuram-carbo-methyl, $(\text{NH}^2\text{CS})_2\text{C}(\text{CH}^3)_2$. When carbothialdine is decomposed with potash, and the liquid is mixed with sal-ammoniac, evaporated down, and treated with cupric sulphate, cupric thiocyanate is precipitated in quantity corresponding with the equation, $\text{C}^2\text{H}^4\text{N}^2\text{S}^2 + 2\text{H}^2\text{O} = \text{CNS.NH}^2 + \text{H}^2\text{S} + 2\text{C}^2\text{H}^4\text{O}$ (Mulder).

With benzaldehyde ammonium thiocarbamate forms stellate groups of colourless crystals, or if too much benzaldehyde has not been added, a perfectly solidified crystalline mass, which may be freed from excess of benzaldehyde by pressure between bibulous paper. The compound thus formed is *dibenzylidenammonium thiocarbamate*, $\text{NH}^2\text{CS}\cdot\text{SN}(\text{C}^6\text{H}^5)_2$, agreeing in all its properties with that which Quadrat obtained by treating benzaldehyde with carbon disulphide and aqueous ammonia (*Liebig's Annalen*, lxxi. 13). This compound was regarded by Quadrat as thiocyanate of benzoyl (or rather benzenyl), $\text{C}^6\text{H}^5\text{NS} = \text{C}^6\text{H}^5\text{CNS}$. Its alcoholic solution gives in general the reactions of ammonium thiocarbamate. Treated with potash, &c. in the manner above described for carbothialdine, it yields a quantity of copper thiocyanate agreeing with the equation:



that is to say, 20.3 per cent. CNS, whereas Quadrat's formula would give 39.4 per cent. (Mulder).



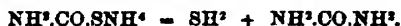
is obtained by fusing thiocarbamide (sulphurea) with succinic anhydride at 140° , and purified by washing the product with alcohol and recrystallising it from glacial acetic acid or from water. It is a yellowish powder composed of crystalline scales, melting at $210.5^\circ\text{--}211^\circ$, and in other respects resembling succinocarbamic acid. On boiling its alkaline solution, it is resolved into succinic acid and thiocarbamide, which immediately suffers further decomposition.

CITRACOTHIOCARBAMIC ACID, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2\text{S} = \text{C}^6\text{H}^4\text{N}^2\text{C} \begin{array}{l} \text{COOH} \\ \text{CO—NH—CS—NH}^2 \end{array}$ *, is prepared by heating citraconic anhydride with thiocarbamide to* 130° *. The crude product, washed and recrystallised from water, yields the pure citracothiocarbamic acid as a white crystalline powder, very much resembling succinotHIocarbamic acid, and melting at* $222^\circ\text{--}223^\circ$ *(Pike,* *Deut. Chem. Ges. Ber.* vi. 1104).

Oxythiocarbamic Acid, $\text{CH}^2\text{NOS} = \text{NH}^2\text{CO.SH}$. The ammonium salt of this acid, discovered by Berthelot (*1st Suppl.* 468), is formed by passing carbon oxysulphide into alcohol saturated with ammonia. The liquid becomes turbid after a while, and solidifies to a pulp of fine white crystals, which must be collected on a filter and washed quickly with ether. It is extremely soluble in water, less soluble in alcohol, insoluble in ether. Dilute acids decompose it, with evolution of carbon oxysulphide, according to the equation:



The aqueous solution is decomposed by heat, with formation of carbonate and sulphide of ammonium. The salt, heated for several hours to $130^\circ\text{--}140^\circ$ in sealed tubes, is resolved into hydrogen sulphide and urea:



This decomposition, which is analogous to that of ammonium carbamate into water and urea, discovered by Basaroff (*1st Suppl.* 1113), shows that oxythiocarbamic acid contains the group CO and not CS (Kretschmar, *J. pr. Chem.* [2], vii. 474).

The solution of the ammonium salt gives with ferric chloride at first a red liquid, and on addition of an excess, a pale red precipitate; with lead acetate a colourless gelatinous precipitate which afterwards turns black; with uranic nitrate a pale yellow precipitate, soluble in excess of the uranic salt; with barium chloride a precipitate on warming (E. Mulder, *Liebig's Annalen*, clixviii. 228).

Action of Aldehydes on Ethylic Oxythiocarbamate or Xanthamide.—Valeral-xanthamide, $C^4H^{10}(NH.CO.SC^2H^5)^2$, is formed on adding strong hydrochloric acid to a mixture of valeral and xanthamide. A gummy mass is thereby produced, which diffuses itself in alcohol without dissolving, and water, added to the liquid throws down a yellowish-white or pure white crystalline powder formed of small, indistinct, coherent plates. This compound has a faint but peculiar odour, dissolves sparingly in ether, more readily in alcohol, and melts at 108° . Heated in the dry state, it gives off an odour of mercaptan, yields ammonia and cyanic acid, and ultimately gives off fetid strongly alkaline vapours.

Chloral and Butyric Chloral likewise unite with xanthamide under the influence of strong hydrochloric acid (Bischoff, *Deut. Chem. Ges. Ber.* vii. 1078).

CARBAMIDE or UREA, $NH^2.CO.NH^2$. *Occurrence in the Animal Body.*—From experiments made on dogs by I. Munk (*Pflüger's Archiv.f. Physiologie*, xi. 100; *Chem. Soc. J.* 1876, i. 89), it appears that the quantity of urea contained in the substance of the liver is less than that in an equal weight of the blood circulating in the tissues; in an average-sized dog, for example, the quantities in the liver and in the blood of the carotid artery were found to be as 0.039 : 0.533. These results are not in accordance with the opinion entertained by some physiologists that the liver is the principal seat of the formation of urea in the animal organism.

According to P. Picard (*Compt. rend.* lxxxiii. 1170; *Chem. Soc. J.* 1877, i. 329), arterial blood contains two substances, which are decomposed by Millon's reagent (mercuric nitrate, v. 952), the one eminently destructible and disappearing almost completely in the capillaries, whereas the other—which is most probably urea—is present in the same proportion in arterial and in venous blood. The nature of the more easily decomposable substance in arterial blood has not yet been made out.

Preparation.—C. A. Bell prepares urea by the action of ammonium sulphate on potassium cyanate obtained by heating the ferrocyanide with potassium dichromate. Well-dried ferrocyanide yields 25 per cent. of its weight of urea (*Chem. News*, xxxii. 99).

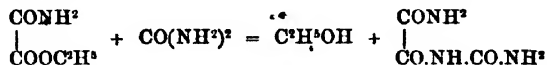
Reactions.—1. When urea is heated over a water-bath with phosphorus trichloride, a violent action takes place, ammonia is eliminated in the form of phosphamide compounds, and biuret is formed, together with an amorphous substance which appears to be triuret. The formation of biuret is represented by the equation :



Phenyl-urea similarly treated yields phenyl-biuret, $NH[CONH(C^6H^5)]^2$ (Weith, *Deut. Chem. Ges. Ber.* x. 1743).

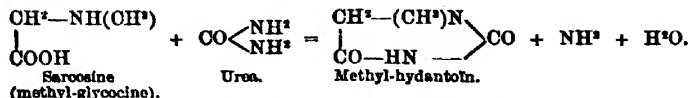
2. When urea is treated with propyl alcohol dissolved in ether, the products formed are propyl-urethane, $C^4H^9NO^2$ (p. 385), and propyl allophanate, $C^6H^{10}N^2O^3$, the former or the latter predominating according as the propyl alcohol or the urea is in excess. Propyl allophanate forms nacreous laminæ, slightly soluble in cold, easily in hot water, still more readily in alcohol, and melting at 150° – 160° (Cahours, *Compt. rend.* lxxvi. 1387).

3. Urea fused with oxamethane yields oxaluramide (oxalan), according to the equation :



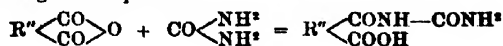
(Carstanjen, *J. pr. Chem.* [2], ix. 143).

4. Urea fused with sarcosine forms methyl-hydantoin, $C^4H^6N^2O$, identical with that which is formed, together with sarcosine, by boiling creatine or creatinine with baryta-water :



Other amido-acids react with urea in a similar manner, forming hydantoin or an analogous substance: thus leucine fused with urea yields a compound crystallising in needles, which appears to be uramidocaproic acid (Huppert, *Deut. Chem. Ges. Ber.* vi. 1278).

5. When urea is fused with the anhydrides of bibasic acids, a reaction takes place, represented by the general equation :



the product being a homologue of oxaluric acid. In this manner succinyl-carbamic acid, $C^6H^4N^2O^4$ (p. 386), is formed from urea and succinic anhydride.

Citraconic anhydride does not unite with urea in this manner; for when the two bodies are heated together to 115° , carbon dioxide is given off, and citraconimide is produced. With thio-urea, on the other hand, citraconic anhydride yields citracothio-carbamic acid (p. 387).

Lactide heated with urea or with thio-urea is converted into lactamide, with evolution of CO^2 or COS (W. H. Pike, *Deut. Chem. Ges. Ber.* vi. 1104).

Detection of Urea.—Musculus (*Compt. rend.* lxxviii. 132) employs for this purpose paper on which urinary ferment has been deposited. This paper is prepared by filtering urine in a state of ammoniacal putrefaction through a paper filter, which is afterwards washed and dried at $35^\circ-40^\circ$. To facilitate its use, it may be coloured with turmeric, and dried again. If preserved in well-closed bottles, it appears to retain its action for a long time. On dipping it into a neutral solution containing urea, this compound is converted, by the action of the ferment, into ammonium carbonate, recognisable by the brown colour which it imparts to the turmeric paper.

Estimation by means of Soluble Hypobromites.—Urea is decomposed by soluble hypobromites and hypochlorites, with evolution of nitrogen:



According to this equation, 1 gram of urea should yield 370 c.c. of nitrogen at $0^\circ C.$, and 760 mm. (v. 952). According to Russell a. West, however (*Chem. Soc. J.* 1874, p. 749), the quantity of nitrogen actually evolved (with hypobromite) is always 8 per cent. less than the calculated amount.

The reaction affords a quick and easy method of determining the quantity of urea contained in aqueous solutions, especially in urine, the nitrogen evolved being collected in a graduated tube, and the amount of urea calculated from the measured volume, due attention being given to the correction just mentioned, also to corrections for temperature and the tension of aqueous vapour,* and in exact experiments to the variations of atmospheric pressure.

Sodium hypobromite is a more convenient oxidiser than the hypochlorite, being more effective, and at the same time more stable, as first pointed out by Knop (*J. pr. Chem.* [3], iii. 1). A solution of convenient strength is obtained by dissolving 100 grams of solid caustic soda in 250 c.c. of water and adding 25 c.c. of bromine.

For description and figures of apparatus for carrying out the determination, see Russell a. West (*loc. cit.*); Dupré (*Chem. Soc. J.* 1877, i. 634); Simpson a. O'Keefe (*Ibid.* 838).

Silver-carbamide. When soda-ley is added to a solution of urea mixed with silver nitrate, a silver compound separates in the form of a light yellow precipitate which is gelatinous at first, but after a while becomes firmer, and easy to filter and wash. To this compound Liebig (*Annalen* lxxxv. 289) assigned the formula $2CON^2H^4.3Ag^2O$ (v. 951), but according to E. Müller (*Deut. Chem. Ges. Ber.* vi. 1019) it is a simple derivative of carbamide represented by the formula $CON^2H^4Ag^2$; when heated it gives off ammonia, as observed by Liebig, but does not detonate.

Salts of Hydroxyl-carbamide, $NH^2.CO.NH(OH)$, (1st Suppl. 725). The potassium and sodium salts are precipitated when an alcoholic solution of urea is added to a solution of potassium or sodium ethylate; they are colourless, and often crystalline, but they absorb water greedily from the air and have not been obtained pure. The potassium salt, dried in a current of air, appeared to have the composition $CON^2H^4(OK).CON^2H^4(OH)$. A lead salt, having the composition $(C^2H^3O^2)^2Pb.(N^2CH^3O^2)^2Pb.N^2CH^3O^2$, is obtained when an aqueous solution of sodium-hydroxyl-carbamide is mixed with a solution of lead acetate till the precipitate which forms at first is redissolved: the clear solution then deposits colourless crystals of the salt above formulated. An aqueous solution of the potassium salt mixed with cupric acetate forms a gummy precipitate which becomes olive-green and shining when dry, and may be approximately represented by the formula, $4N^2CH^3O^2.Cu.C^2H^3O^2$ (N. Hodges, *Liebig's Annalen*, clxxxii. 214).

* With Russell a. West's apparatus, and at the temperature of $68^\circ F.$, which is about that of the wards of hospitals, and of rooms in which the experiments are most likely to be made, the tension of the aqueous vapour, together with the expansion of the gas, almost exactly counterbalances the loss of nitrogen in the reaction.

*Substitution-derivatives of Carbamides.**A. Containing Monatomic Alcohol-radicles.*

Diethyl-carbamide, $\text{CH}_3(\text{C}^2\text{H}_5)_2\text{N}^2\text{O}$. The symmetrical modification of this compound $\text{NH}(\text{C}^2\text{H}_5)\cdot\text{CO}\cdot\text{NH}(\text{C}^2\text{H}_5)$, which Hofmann obtained by the action of ethylamine on ethyl-carbimide (ethyl isocyanate, i. 754) is also formed as a bye-product in the preparation of ethyl cyanide. It dissolves readily in water, alcohol, and ether, melts at 107.5° – 110° , and distils without decomposition at 160° (v. Zotta, *Liebig's Annalen*, clxxix. 101). According to Habich a. Limpricht (*ibid.* cv. 395), it melts at 106° and distils at about 250° ; according to Wurtz (*Rép. chim. pure*, iv. 199) it melts at 112.5° and boils at 263° . Heated with potash it yields ethylamine (v. Zotta).

On passing *nitrous acid* into an alcoholic solution of diethyl-carbamide in nitric acid, an oily liquid is formed heavier than water and only slightly soluble therein. This compound decomposes with great violence below 100° , giving off gases and white vapours. When mixed with sand and heated, it gives off carbon dioxide, ethylene, nitrogen, and ethyl-carboxylamine, $\text{CO}=\text{N}-\text{C}^2\text{H}_5$. Heated with nitric acid, it gives off carbon dioxide and yields nitrate of ethylamine. v. Zotta assigns to the oily liquid produced by the action of nitrous acid on diethyl-carbamide, the formula $\text{C}^2\text{H}_5-\text{N}<\begin{smallmatrix} \text{N(OH)} \\ \text{CO} \end{smallmatrix}>\text{N}-\text{C}^2\text{H}_5$. According to Wurtz, on the other hand (*loc. cit.*) the products obtained by the action of nitrous acid on diethyl-carbamide are carbon dioxide, nitrogen, and diethylamine; perhaps, however, the reaction which Wurtz observed took place at a higher temperature.

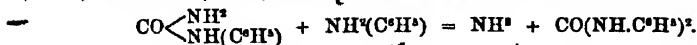
Tetreehyl-carbamide, $\text{N}(\text{C}^2\text{H}_5)_2\cdot\text{CO}\cdot\text{N}(\text{C}^2\text{H}_5)_2$, is formed on passing carboxyl chloride into a solution of diethylamine in ligroin. It boils at 205° , dissolves in acids, and is precipitated from the solutions by alkalis (W. Michler, *Deut. Chem. Ges. Ber.* vii. 1664).

Phenyl-carbamide or **Carbanilamide**, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}(\text{C}^6\text{H}_5)$, is formed by the combination of ammonia with phenyl isocyanate (obtained by distilling diphenyl-carbamide with carbodiphenylimide),—or by the action of potassium cyanate on aniline hydrochloride (Weith, *Deut. Chem. Ges. Ber.* ix. 810). It crystallises in the monoclinic system, exhibiting the faces $\infty P \infty$, $0P$, $-P \infty$, ∞P , ∞R_2 . The crystals are tabular from predominance of the face $\infty P \infty$, according to which they also exhibit very distinct cleavage (Arzruni, *Pogg. Ann.* clii. 284). Melting point, 144° – 145° (Weith).

Diphenyl-carbamide, $\text{CH}_2(\text{C}^6\text{H}_5)_2\text{N}^2\text{O}$. Of this compound there are two modifications, viz.—

Symmetrical (carbanilide)	$\text{NH}(\text{C}^6\text{H}_5)\cdot\text{CO}\cdot\text{NH}(\text{C}^6\text{H}_5)$
Unsymmetrical	$\text{NH}_2\cdot\text{CO}\cdot\text{N}(\text{C}^6\text{H}_5)_2$

a. *Carbanilide* (i. 756) is formed: 1. By heating dry monophenyl-carbamide (1 mol.) with aniline (1 mol.) to 180° – 190° , as long as ammonia continues to be evolved:—



The radio-crystalline product of the reaction is washed, first with very dilute hydrochloric acid, then with hot water, and finally with cold alcohol; and the residue recrystallised from alcohol yields pure carbanilide, amounting to 96 per cent. of the calculated quantity (Weith, *Deut. Chem. Ges. Ber.* ix. 820).

2. Together with alcohol and acetone, by heating aniline for a short time with ethylic aceto-acetate:



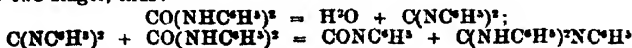
The carbanilide thus produced may be freed from alcohol by distillation (Oppenheim a. Precht, *ibid.* 1098).

Carbanilide is resolved by heating with *alcoholic ammonia* into carbamide and aniline:



(Claus, *ibid.* 693).

Heated for four or five hours with *phosphorus trichloride*, it yields phenyl isocyanate with traces of hydrochloride of triphenyl-guanidine, the reaction apparently taking place by two stages, thus:



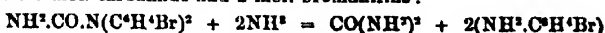
(Weith, *ibid.* 810).

B. Unsymmetrical Diphenyl-carbamide, $\text{NH}^1\text{CO.N}(\text{C}^6\text{H}^5)^2$.—When carbonyl chloride (phosgene) is slowly passed to saturation into a solution of diphenylamine in chloroform, diphenylamine hydrochloride separates out, and the filtrate when evaporated leaves diphenylcarbamic chloride, $\text{Cl.CO.N}(\text{C}^6\text{H}^5)^2$, as a bluish salt which crystallises from alcohol in white scales; and this chloride, heated with alcoholic ammonia in a sealed tube to a temperature not exceeding 100° , is converted into unsymmetrical diphenyl-carbamide. This compound crystallises from alcohol in long needles melting at 189° . It is resolved by heat into cyanic acid and diphenylamine: $\text{NH}^2\text{CO.N}(\text{C}^6\text{H}^5)^2 = \text{CONH} + \text{NH}(\text{C}^6\text{H}^5)^2$. Distilled with solid potassium hydrate it is completely resolved into carbon dioxide, ammonia, and diphenylamine:



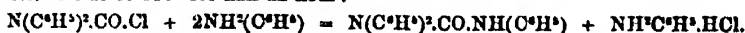
Heated with sulphuric acid it forms a blue solution (Michler, *Deut. Chem. Ges. Ber.* ix. 396).

Bromodiphenyl-carbamide.—Diphenyl-carbamide [unsymmetrical] is capable of taking up [by substitution] 6 atoms of bromine, but the only one of the resulting derivatives hitherto isolated is a dibromophenylcarbamide, in which the two bromine-atoms are situated in different phenyl-groups, as represented by the formula $\text{NH}^1\text{CO.N} \begin{smallmatrix} \text{C}^6\text{H}^4\text{Br} \\ \text{C}^6\text{H}^4\text{Br} \end{smallmatrix}$. This compound, heated with alcoholic ammonia, is completely resolved into 1 mol. carbamide and 2 mol. bromaniline:

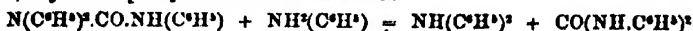


(Claus a. Henn, *Liebig's Annalen*, clxxix. 120).

Triphenyl-carbamide, $\text{NH}(\text{C}^6\text{H}^5)\text{CO.N}(\text{C}^6\text{H}^5)^2$, is formed, together with aniline hydrochloride, by heating diphenylcarbamic chloride dissolved in chloroform with 2 mol. aniline to 130° for half an hour:—



It crystallises in white needles, melts at 136° , forms a deep blue solution with hot strong sulphuric acid, and is resolved, by distillation with solid potassium hydrate, into aniline, diphenylamine, and carbon dioxide. Heated to 160° with excess of aniline, it yields diphenylamine and carbanilide:



(Michler, *Deut. Chem. Ges. Ber.* ix. 396).

Tetraphenyl-carbamide, $\text{N}(\text{C}^6\text{H}^5)^3\text{CO.N}(\text{C}^6\text{H}^5)^2$, is obtained by heating diphenylamine (more than 2 mol.) with chlorodiphenyl-carbamic acid (1 mol.) to 200° – 220° in closed tubes for several hours. From the product mixed with chloroform the excess of diphenylamine may be precipitated by dry hydrogen chloride; and on evaporating the filtrate, tetraphenyl-carbamide remains, contaminated with a red colouring matter, from which it may be freed by washing with alcohol (Michler). Tetraphenylcarbamide is also formed as a secondary product in the preparation of diphenylcarbamic chloride by the action of carbonyl chloride on diphenylamine (Girard a. Willm, *Bull. Soc. Chim.* [2], xxv. 248). It dissolves easily in boiling alcohol and melts at 183° (Michler), at 178° – 180° (Girard a. Willm). When heated to 250° with hydrochloric acid, it is resolved into diphenylamine and carbon dioxide.

Phenyl-ethyl-carbamide Chloride, or **Ethyl-phenyl-carbamic Chloride**, $\text{Cl.CO.N}(\text{C}^2\text{H}^5)(\text{C}^6\text{H}^5)$, produced by the action of carbonyl chloride on ethylaniline, forms small white needles melting at about 52° .

Diphenyl-diethyl-carbamide, $\text{N}(\text{C}^2\text{H}^5)^2\text{CO.N}(\text{C}^6\text{H}^5)^2$, obtained by gradually adding an excess of diethylamine to a cooled solution of diphenylcarbamic chloride in chloroform, has a peculiar odour, dissolves easily in alcohol, is insoluble in water, and forms small laminar crystals melting at 54° . By distillation with potassium hydrate it is resolved into diethylamine, diphenylamine, and carbon dioxide.

An isomeric diphenyl-diethyl-carbamide, $\text{N}(\text{C}^2\text{H}^5)(\text{C}^6\text{H}^5)\text{CO.N}(\text{C}^2\text{H}^5)(\text{C}^6\text{H}^5)$, prepared from phenyl-ethyl-carbamic chloride and ethylaniline, is insoluble in water, soluble in hot alcohol, and melts at 79° .

Triphenyl-ethyl-carbamide, $\text{N}(\text{C}^6\text{H}^5)^2\text{CO.N}(\text{C}^2\text{H}^5)(\text{C}^6\text{H}^5)$, from diphenylamine and phenyl-ethyl-carbamic chloride, crystallises in small needles.

All the carbamides containing the group $\text{N}(\text{C}^6\text{H}^5)^2$ exhibit, when heated with strong sulphuric acid, the blue coloration characteristic of diphenylamine (Michler).

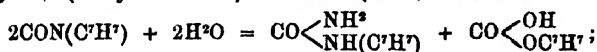
Diphenyl-paratolyl-carbamide, $\text{N}(\text{C}^6\text{H}^4)^2\text{CO.NH}(\text{C}^6\text{H}^4.\text{CH}^3)$, from diphenylcarbamic chloride and paratoluidine, forms white needles melting at 130° . Heated with toluidine to a temperature above 130° , it yields ditolylcarbamide, $\text{CO}(\text{NH.C}^6\text{H}^4)^2$.

(m. p. 256°), and diphenylcarbamide. A carbamide prepared from carbonyl chloride and paratoluidine was also found to melt at 256°. Diphenyl-tolyl-carbamide distilled with potassium hydrate is resolved into diphenylamine, toluidine, and carbon dioxide (Michler).

Orthotoluidine reacts with diphenylcarbamide in the same manner as paratoluidine.

Phenylene-carbamide, $C^6H^4 \begin{smallmatrix} \text{NH.CO.NH}^2 \\ \text{NH.CO.NH}^2 \end{smallmatrix}$ obtained by digesting phenylene-diamine hydrochloride with potassium cyanate, forms crystals, usually of a reddish colour, which dissolve sparingly in alcohol. When heated above 300°, it melts and sublimes in small needle-shaped crystals (R. B. Warder, *Deut. Chem. Ges. Ber.* viii. 1180).

Benzyl-carbamides, or Benzyl-ureas. *Mono- and Di-benzyl-carbamide*, $CH^3(C^6H^5)N^2O$ and $OH^2(C^6H^5)^2N^2O$, are formed simultaneously by heating urea or potassium cyanate with benzyl chloride and alcohol in a reflux apparatus, and are separated by water, which dissolves only the former (Cannizzaro, *2nd Suppl.* 181). Monobenzyl-carbamide is also formed, together with acid benzyl carbonate, by heating benzyl isocyanate (benzyl-carbimide) with water (Letts, *Chem. Soc. Jour.* 1872, 449):



and, without any other organic compound, by mixing the warm solutions of potassium cyanate and benzylamine hydrochloride in molecular proportions, and boiling for a short time (Paternò a. Spica, *Gazzetta chimica italiana*, v. 388). It crystallises in colourless needles, melting at 147°–147.5°.

Dibenzyl-carbamide, $CON^2(C^6H^5)^2H^2$.—The *symmetrical modification*, $CO \begin{smallmatrix} \text{NH.C}^6H^5 \\ \text{NH.C}^6H^5 \end{smallmatrix}$, is formed by heating urea with benzyl-alcohol to 200°:



at 130°–140° benzyl carbamate is formed, together with a crystalline body not yet fully examined, which melts at 151°–152.5° (Campani a. Amato, *Gazzetta*, i. 39). The same dibenzyl-carbamide is formed from the corresponding thiocarbamide by desulphuration in alcoholic solution with mercuric oxide (Strakosch, *Deut. Chem. Ges. Ber.* v. 692); also, together with mono-benzyl-carbamide, by the processes already mentioned. It melts at 167° (Paternò a. Spica).

The *unsymmetrical modification*, $CO \begin{smallmatrix} \text{NH}^2 \\ \text{N}(C^6H^5) \end{smallmatrix}$, formed by treating potassium cyanate with dibenzylamine hydrochloride in molecular proportion, crystallises in large hard shining prisms, slightly soluble in cold water and melting at 124°–125° (Paternò a. Spica, *Gazzetta*, v. 388).

Cymyl-carbamide, $C^{11}H^{16}N^2O = NH^2.CO.NH(C^{10}H^{15})$, also called *Cumenyl-urea*, is formed by the action of ammonia on cymyl cyanate. When cymyl chloride (prepared from cymyl alcohol and hydrochloric acid) is heated for a few minutes with excess of silvercyanate, and then distilled, cymyl cyanate passes over as a yellowish liquid, clear at first, but quickly becoming turbid and gradually thickening, evidently from formation of cyanurate. The freshly prepared cyanate in contact with ammonia solidifies to a crystalline mass of cymyl-carbamide, which crystallises from boiling water in small shining needles, melting at 133°, and dissolving easily in boiling water, alcohol, and ether.

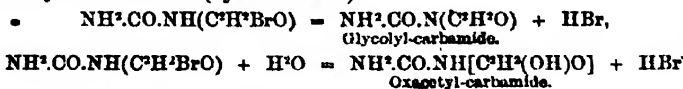
Cymyl-carbamide distilled alone, or cymyl cyanate distilled with potash, yields cymylamine, $C^{10}H^{15}.NH^2$, which, when mixed with carbon disulphide, solidifies, with great rise of temperature, to a crystalline pulp, probably consisting of cymylthiocarbamate of cymylamine; and this last compound treated with mercuric chloride, yields cymyl isocyanate or cymyl-carbimide, $CS=N-C^{10}H^{15}$ (A. Raab, *Deut. Chem. Ges. Ber.* viii. 1151).

Phenyl-cymyl-carbamide, $C^{11}H^{15}N^2O = C^6H^5.NH.CO.NH.C^{10}H^{15}$, prepared like cymyl-carbamide, with aniline instead of ammonia, forms small needles melting at 140°, insoluble in water, slightly soluble in cold, more freely in warm alcohol (Raab).

B. *Derivatives containing Acid-radicles.*

Acetyl-carbamide, $\text{NH}^2\text{CO.NH}(\text{C}^2\text{H}^3\text{O})$, is obtained by heating the corresponding thiocarbamide in aqueous solution with mercuric cyanide; hydrocyanic acid is then given off, mercuric sulphide is precipitated, and the filtrate on evaporation leaves acetyl-carbamide (Nencki a. Leppert, *Deut. Chem. Ges. Ber.* vi. 906. See also i. 733; 1st Suppl. 1116).

Bromacetyl-carbamide, $\text{NH}^2\text{CO.NH}(\text{C}^2\text{H}^3\text{BrO})$, prepared by mixing 3 parts of urea with 5 parts of bromacetyl bromide and recrystallising the product from dilute alcohol, forms needles slightly soluble in cold water, decomposed by boiling water and alkalis. By ammonia it is converted either into glycolyl-carbamide (hydantoin) or oxacetyl-carbamide (hydantoic acid):—



(Bayer, *Liebig's Annalen*, cxxx. 129).

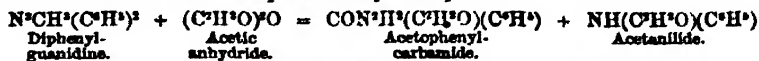
According to E. Mulder, on the other hand (*Deut. Chem. Ges. Ber.* vi. 1016), when bromacetyl-carbamide is heated to 100° in sealed tubes with alcoholic ammonia, or when dry ammonia gas is passed through an alcoholic solution of bromacetyl-carbamide heated to 70° – 80° , the chief product is diglycolamido-diuramide, $(\text{NH}^2\text{CO.NH.CO.CH}^2)^2\text{NH}$, which melts at 195° – 200° , dissolves sparingly in cold, with moderate facility in warm water, and crystallises in slender needles. With aqueous ammonia different products are obtained.

Chloracetyl-carbamide, $\text{NH}^2\text{CO.NH}(\text{C}^2\text{H}^2\text{ClO})$, is prepared by mixing 1 mol. urea with 1 mol. chloracetyl chloride (1st Suppl. 1116). A brisk reaction then takes place, attended with evolution of hydrogen chloride, after which the mixture must be heated on the water-bath for several hours. The sublimate thereby obtained is washed with cold water, pressed, and crystallised several times from alcohol with the aid of animal charcoal.

Chloracetyl-carbamide crystallises in thin colourless needles, insoluble in cold, slightly soluble in boiling water, moderately soluble in hot alcohol of 40 per cent. It begins to decompose at 160° , a small quantity, however, subliming without decomposition and forming white silky needles. It is decomposed by fuming nitric acid; dissolved without decomposition by warm concentrated nitric acid, also by sulphuric, hydrochloric, and acetic acids. It is not precipitated by mercurous nitrate or silver nitrate. With nascent hydrogen it yields, not acetyl-carbamide and hydrochloric acid, but another body, which is crystallisable and easily soluble in cold water (Tommasi, *Compt. rend.* lxxvi. 640).

Trichloracetyl-carbamide, $\text{NH}^2\text{CO.NH}(\text{C}^2\text{Cl}^3\text{O})$, is obtained by gently boiling 1 part of urea with 15 parts of trichloroacetyl chloride, heating the product, as soon as it begins to solidify, in order to drive off the excess of trichloroacetyl chloride and the hydrochloric acid produced, and crystallising the residual white mass from alcohol. It forms white silky needles soluble in boiling water, but decomposing at the same time, with formation of a substance not yet investigated; soluble also in warm aniline. It melts at 150° , partly subliming and decomposing at the same time, and decomposing with an odour of acetic acid. It is decomposed by boiling with soda-ley, and with alcoholic ammonia. Phosphorus trichloride does not act upon it at ordinary temperatures; but hot strong nitric acid decomposes it with great energy and rapid evolution of gas. Moist silver oxide and lead oxide withdraw the chloride, forming salts soluble in cold water. Mercuric nitrate precipitates the aqueous solution (Meldola a. Tommasi, *Chem. Soc. Jour.* 1874, 404).

Acetophenyl-carbamide, $\text{CON}^2\text{H}(\text{C}^2\text{H}^3\text{O})(\text{C}^6\text{H}^5)$, is formed by heating monophenyl-carbamide, or diphenyl-guanidine, with acetic anhydride to 100° . The reaction in the latter case is represented by the equation:



On treating the oily product of this reaction with boiling water, the acetophenyl-carbamide is dissolved, and separates in needles on cooling. After repeated crystallisation from alcohol, it melts constantly at 183° (D. M'Craith, *Deut. Chem. Ges. Ber.* viii. 1181).

Acetodiphenyl-carbamide or Aceto-carbanilide, $\text{CON}^2\text{H}(\text{C}^2\text{H}^3\text{O})(\text{C}^6\text{H}^5)^2$, is formed, together with acetamide and a small quantity of carbon dioxide (resulting

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from partial decomposition of the product) by heating diphenyl-guanidine with acetic anhydride to 150°:



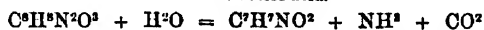
The dark brown liquid product dissolves almost completely in boiling water, and the solution on cooling deposits the acetodiphenyl-carbamide in fine crystalline laminae. When purified by recrystallisation from alcohol it melts at 115° (M'Creaht).

Benzoyl-carbamides (Nitro- and Amido-). Metanitrobenzoyl-carbamide, $NH^2.CO.NH[C^6H^4(NO^2)O]$, prepared by the action of metanitrobenzoyl chloride on urea, is converted by boiling with ammonium sulphide into metamidobenzoyl-carbamide, $C^6H^5N^2O^2 = NH^2.CO.NH[C^6H^4(NH^2)O]$. This compound forms slender needles having a bitter taste, moderately soluble in hot water and hot alcohol, insoluble in ether. When heated to 200°, it is converted into a neutral substance. Its solution in potash is precipitated both by carbonic acid and by mercuric chloride. Its hydrochloride forms white needles containing 1 mol. water of crystallisation.

Both metamidobenzoyl-carbamide and the isomeric body, benzoglycocyamine, or benzcreatine (2nd Suppl. 130), when heated with baryta-water, give off carbon dioxide and ammonia; and if the boiling be continued till ammonia is no longer evolved, they yield, as final product, amidobenzoic acid; but if the boiling be interrupted at an earlier stage, the product consists of the intermediate body, uramidobenzoic or benzhydantoic acid (1st Suppl. 318):

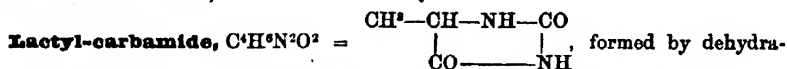


Uramido-
benzoic acid.



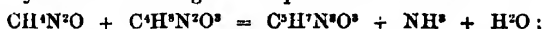
Amidoben-
zoic acid.

Metamidobenzoyl-carbamide, boiled with dilute acids, is resolved into amidobenzoic acid and urea: $C^6H^5N^2O^2 + H^2O = C^6H^5NO^2 + CH^2N^2O$. Benzoglycocyamine is not attacked by hydrochloric acid, either dilute or concentrated (Griess, *Deut. Chem. Ges. Ber.* viii. 221).



tion of lacturamic acid, $C^6H^5N^2O^3$, has been already described (2nd Suppl. 723).

Maly-carbamide, $C^6H^5N^2O^3 = CH(C^6H^5O^2)^2N^2O$. When urea is treated with asparagin, a body is formed having the composition $C^6H^5N^2O^3$:



and this substance heated with nitric or hydrochloric acid is converted, by removal of NH^3 , into maly-carbamide, which crystallises in prisms, melts with decomposition at 215°–220°, and forms salts, all of which, excepting the silver salt, are very soluble in water.

Maly-carbamide treated with bromine yields substitution-products, varying in composition according to the conditions of the experiment. Five of these have been isolated, and the following formulæ have been ascribed to them:



The last of these bodies crystallises in hard shining hexagonal crystals, moderately soluble in alcohol and ether, and decomposed by prolonged heating at 100°. This substance, as well as (2), is converted by ammonia into a body resembling murexid (Grimaux, *Bull. Soc. Chim.* [2], xxiv. 337).

Succinyl-dicarbamide, $C^6H^5N^2O^4 = C^6H^4(CO.NH.CO.NH)^2$, is prepared by very carefully heating 2 mols. urea with rather more than 1 mol. succinyl chloride to 60°–70°, washing the resulting mass with warm alcohol, and drying it over sulphuric acid. It is a white bulky powder, nearly insoluble in alcohol and ether, very slightly soluble in hot water. It dissolves in cold potash-ley apparently without decomposition, but when boiled therewith it is resolved into CO^2 , NH^3 , and succinic acid, the first products of the reaction being probably succinic acid and urea (Conrad, *J. pr. Chem.* [2], ix. 300).

THIOCARBAMIDE, OF SULPHUREA, AND ITS DERIVATIVES.

Thiocarbamide, $\text{CSN}^2\text{H}^4\text{NH}^2\text{CS.NH}^2$. This compound, which Reynolds obtained by the molecular transformation of ammonium thiocyanate (1st Suppl. 1116), is also produced by the action of dry hydrogen sulphide on anhydrous cyanamide, either in the fused state or dissolved in anhydrous ether: in the latter case the passage of the gas must be continued for two days. The formation of thiocarbamide in the ethereal solution is retarded by the presence of acids, but greatly accelerated by ammonia. Ammonium sulphide converts cyanamide in aqueous solution into thiocarbamide even at ordinary temperatures, and without simultaneous formation of dicyanodiamide. The salts of cyanamide (cyanamides) are acted upon by hydrogen sulphide in the same manner as cyanamide itself. Dry hydrogen sulphide acts with great violence on silver cyanide (E. Baumann, *Deut. Chem. Ges. Ber.* viii. 26).

Nitrous acid converts thiocarbamide into a reddish body, with evolution of nitrogen dioxide and probably of free nitrogen. *Nitrous ether* converts it into ammonium thiocyanate (Claus, *Liebig's Annalen*, clxxix. 135).

Thiocarbamide and *trichloroacetic acid* heated together on the water-bath or in a sealed tube, yield chiefly hydrogen sulphide and carbon dioxide, perhaps also chloroform and volatile organic compounds; a similar reaction takes place in alcoholic solution (Maly, *Deut. Chem. Ges. Ber.* ix. 173). With *monochloroacetic acid*, thiocarbamide yields thiohydantoin (Claus u. Hermes, *Liebig's Annalen*, clxxix. 145). Thiocarbamide treated in aqueous solution with *silver carbamide* is converted into cyanamide and urea, with separation of silver sulphide. If the silver carbamide used is quite fresh, another product is also formed which has not yet been investigated (Ponomareff, *Bull. Soc. Chim.* [2], xxi. 546).

Compounds.—Thiocarbamide unites directly with bromine and chlorine.

The *bromide*, $(\text{CSN}^2\text{H}^4)^2\text{Br}^2$, is formed, with violent reaction, when 1 mol. bromine is added to a concentrated alcoholic solution of 1 mol. thiocarbamide. The crystals thus obtained dissolve without alteration in alcohol, are insoluble in ether, and are decomposed when heated alone to 75° , or with bromine. The aqueous solution when heated deposits sulphur. Sodium-amalgam added to the alcoholic solution reproduces thiocarbamide.

The *chloride*, $(\text{CSN}^2\text{H}^4)^2\text{Cl}^2$, obtained by the action of chlorine on a concentrated alcoholic solution, may be washed with ether and dried at 90° – 100° . With careful cooling, both these compounds may be prepared in aqueous solution (Claus, *Liebig's Annalen*, clxxix. 135).

2. With ethyl bromide and iodide.—Thiocarbamide heated with *ethyl bromide* yields the compound $\text{CSN}^2\text{H}^4\cdot\text{C}^2\text{H}^5\text{Br}$, which crystallises in hexagonal plates and is easily decomposable (Claus u. Stegried, *ibid.* 145). With *ethyl iodide*, according to the conditions of the experiment, the compounds $\text{CSN}^2\text{H}^4\cdot\text{C}^2\text{H}^5\text{I}$ and $2\text{CSN}^2\text{H}^4\cdot\text{C}^2\text{H}^5\text{I}$ are obtained; similar products also with *acetyl chloride* (Claus u. Hermes, *ibid.*)

With metallic chlorides.—The compound $(\text{CSN}^2\text{H}^4)^2\cdot\text{AgCl}$ is precipitated on mixing a dilute solution of thiocarbamide with *silver nitrate* till the turbidity at first produced disappears, and then adding *hydrochloric acid*. This compound is not decomposed by boiling water containing hydrochloric acid, but pure water at the boiling heat decomposes it, with separation of silver sulphide. Strong nitric acid separates silver chloride. Warm aqueous ammonia withdraws the whole of the silver in the form of the sulphide, producing at the same time sulphur and dicyanodiamidine (Baumann, *loc. cit.*) With *lead chloride*, thiocarbamide forms the compound $(\text{CSN}^2\text{H}^4)^2\cdot\text{PbCl}^2$, which crystallises in needles, and a single double salt with *mercurous chloride* (Claus, *Liebig's Annalen*, clxxix. 135). With *mercuric chloride*, thiocarbamide unites in two proportions, yielding the compound $4\text{CSN}^2\text{H}^4\cdot\text{HgCl}^2$, which forms large well-defined crystals, and $2\text{CSN}^2\text{H}^4\cdot\text{HgCl}^2$, which is a chalky powder. These two compounds are likewise formed, together with metallic mercury, on heating thiocarbamide with mercurous chloride (Claus, *Deut. Chem. Ges. Ber.* ix. 227). According to Maly (*ibid.* 173), the latter compound crystallises in tufts of microscopic needles, very slightly soluble in water (a $\frac{1}{10}$ per cent. solution giving a considerable precipitate), insoluble in alcohol, hydrochloric acid, and salt-water. Aqueous sodium carbonate decomposes it, even at ordinary temperatures, with formation of mercuric sulphide.

The *sine compound*, $2\text{CSN}^2\text{H}^4\cdot\text{ZnCl}^2$, formed on mixing the aqueous solutions of thiocarbamide and zinc chloride, is moderately soluble in warm water, and crystallises in large colourless prisms having a glassy lustre, and mostly grouped in spherical geodes. Hydrogen sulphide passed into its solution throws down sulphide of zinc.

Nitric acid oxidises the compound with violence. The compound of thiocarbamide with *stannous chloride* has the composition $2\text{CSN}^2\text{H}^4.\text{SnCl}^2$ (Maly).

With other metallic salts.—With *mercurio iodide*, thiocarbamide forms the compound $\text{CSN}^2\text{H}^4.\text{HgI}^2$, which crystallises in yellow needles, insoluble in water and in acid liquids, but easily soluble in alcohol. With *cadmium sulphate* it forms the salt $2\text{CSN}^2\text{H}^4.\text{CdSO}^4$, which crystallises in short white prisms, or longer transparent and colourless prisms, moderately soluble in water (Maly).

Thiocarbamide and recently precipitated *silver oxalate* (1 mol. of each) heated together in aqueous solution to about 100° , yield silver sulphide, cyanamide, and oxalic acid (Maly). According to Claus (*loc. cit.*) a solution of thiocarbamide boiled with *silver oxalate* yields metallic silver, silver sulphide, and the compound $6\text{CSN}^2\text{H}^4.\text{C}^2\text{O}^4\text{Ag}^2$, which crystallises from hot water in glassy needles, very slightly soluble in cold water. It has a neutral reaction; decomposes at 60° , with separation of silver; is decomposed by hydrogen sulphide into oxalic acid, silver sulphide, and thiocarbamide, and partially decomposed by prolonged boiling with water, this decomposition, as also the reaction between thiocarbamide and silver oxalate, being attended with evolution of carbon dioxide (Maly).

Substitution-derivatives of Thiocarbamide.

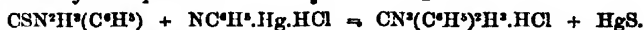
A. Containing Monatomic Alcohol-radicles.

Allyl-ethyl-thiocarbamide, $\text{CSN}^2\text{H}^2(\text{C}^3\text{H}^3)(\text{C}^2\text{H}^5)$, formed by the action of allyl-thiocarbimide on ethylamine, crystallises with difficulty, and is slowly desulphurised by mercuriophenyl ammonium chloride, yielding a salt which crystallises from water in efflorescent tablets, containing the elements of 1 mol. ethyl-phenyl-guanidine and 1 mol. mercuric chloride, and therefore represented by the formula $\text{CN}^4(\text{C}^6\text{H}^5)(\text{C}^2\text{H}^5)(\text{C}^3\text{H}^3)\text{H}^2.\text{HgCl}^2$ (Forster, *Deut. Chem. Ges. Ber.* vii. 294).

Amyl-thiocarbamide, $\text{NH}^2.\text{CS}.\text{NH}(\text{C}^5\text{H}^{11})$. This compound forms monoclinic crystals, exhibiting the faces 0P , ∞P , $-\text{P}$, $\frac{1}{2}\text{R}\infty$. The crystals are tabular, from predominance of 0P , and cleave perfectly in the direction of this face, less distinctly parallel to ∞P . The plane of the optic axes is the plane of symmetry (Arzruni, *Pogg. Ann.* clii. 284).

Phenyl-thiocarbamide, $\text{C}^6\text{H}^5\text{N}^2\text{S} = \text{NH}^2.\text{CS}.\text{NH}(\text{C}^6\text{H}^5)$, is formed by the action of hydrogen sulphide on cyananilide dissolved in benzene, and crystallises out even while the gas is passing through the liquid: $\text{CN}.\text{NH}.\text{C}^6\text{H}^5 + \text{H}^2\text{S} = \text{NH}^2.\text{CS}.\text{NH}(\text{C}^6\text{H}^5)$ (Weith a. Weber, *Deut. Chem. Ges. Ber.* viii. 819). Phenyl-thiocarbamide may also be prepared by heating aniline hydrochloride and ammonium thiocyanate (1 mol. of each) on the water-bath for a few hours, evaporating to dryness, again heating the residue for some hours, and treating the melt with water, which leaves the phenyl-thiocarbamide undissolved (Ph. de Clermont, *Compt. rend.* lxxiii. 512).

This compound, heated with *ammonia* to 130° – 140° , is resolved into ammonium thiocyanate and aniline. Heated with *hydrochloric acid* to 120° in a sealed tube, it is resolved into carbon dioxide, ammonia, hydrogen sulphide, and aniline. Heated by itself to 180° in a sealed tube, it splits up into diphenyl-thiocarbamide, ammonia, aniline, and other products (de Clermont). Boiled in alcoholic solution with *mercuriophenylammonium chloride*, it is very slowly desulphurised, and converted, after several days' boiling, into diphenyl-guanidine, the formation of which is preceded by that of intermediate products containing sulphur and mercury. The final reaction is represented by the equation:



Diphenyl-thiocarbamide or **Thiocarbamilide**, $\text{CS}(\text{NH}.\text{C}^6\text{H}^5)^2$. This compound, added by small portions to *fuming nitric acid*, is very strongly attacked; and on pouring the resulting solution into water, boiling the nitro-compound which separates out with alcohol, and recrystallising the undissolved residue from strong nitric acid, yellow crystals are obtained having the composition of tetranitro-azoxybenzene, $\text{C}^{12}\text{H}^4(\text{NO}^2)^4\text{N}^2\text{O}$. Diphenyl-thiocarbamide is oxidised by chromic acid and permanganic acid, probably yielding phenyl-thiocarbimide and diphenyl-carbamide (m. p. about 228°). On heating diphenyl-thiocarbamide with strong sulphuric acid, sulphur dioxide and carbon oxysulphide are given off. The product diluted with water and saturated with potash, yields a large quantity of aniline; when neutralised with barium carbonate and evaporated, it yields only traces of a barium salt (A. Fleischer, *Deut. Chem. Ges. Ber.* ix. 993).

Diphenyl-thiocarbamide boiled in alcoholic solution with *mercuriophenyl-ammonium chloride*, as long as mercuric sulphide separates out, is decomposed in the same

manner as monophenyl-thiocarbamide, yielding the hydrochloride of triphenyl-guanidine, which remains on evaporating the alcoholic filtrate (Forster, *ibid.* vii. 294).



On the reaction of Diphenyl-thiocarbamide with Carbodiphenylimide, see p. 402.

Di-parachlorophenyl-thiocarbamide,



(Losanitsch, *Deut. Chem. Ges. Ber.* v. 156; Beilstein a. Kurbatow, *ibid.* vii. 730, 1489, 1650).—This compound, prepared by boiling *p*-chloraniline (from chloracetanilide) with carbon disulphide, crystallises from alcohol in long white needles, having a bitter taste and melting at 166° (Losanitsch), at 168° (B. and K). On mixing its hot alcoholic solution with iodine dissolved in alcohol, sulphur immediately separates out; the remaining liquid distilled in a current of steam yields chlorophenyl-thiocarbimide, $\text{SC}=\text{N}-\text{C}^6\text{H}_4\text{Cl}$; and the residue of the distillation contains a small quantity of a substance soluble in alkali, precipitable therefrom by acids, and probably consisting of trichloro-triphenyl-guanidine, $(\text{C}^6\text{H}_4\text{Cl})\text{N}=\text{C}(\text{NH}\cdot\text{C}^6\text{H}_4\text{Cl})^2$ (Losanitsch). According to Beilstein a. Kurbatow, this reaction yields, in addition to the products above mentioned, di-parachlorophenylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}^6\text{H}_4\text{Cl})^2$, chlorophenyl-thiourethane, $\text{CS}\cdot\text{O}\cdot\text{C}^6\text{H}_4\text{Cl}$, and parachloraniline hydriodide.

(1). On adding iodine in theoretical quantity to a boiling alcoholic solution of di-parachlorophenyl-thiocarbamide, the liquid ultimately becomes colourless, and yields, when heated with water, a distillate of chlorophenyl-thiocarbimide, which crystallises from alcohol in long shining needles melting at 45°–47° (at 40° according to Losanitsch). (2). The remaining distillation-water contains nothing but parachloraniline hydriodide. (3). When the resinous mass which remains after distillation with water, is boiled with soda-ley as long as the resulting alkaline solution gives a precipitate with hydrochloric acid, the whole of this alkaline liquid then treated with the acid, and the precipitate crystallised from ligroin, parachlorophenyl-thiourethane is obtained, in needles melting at 102.5°. The same compound is produced directly by heating chlorophenyl-thiocarbamide with alcohol to 140°. (4). When the portion of the resinous mass which is insoluble in soda-ley is exhausted with alcohol, and the residue, after digestion with carbon disulphide, to remove free sulphur, is recrystallised from glacial acetic acid, di-*p*-chlorophenyl-carbamide, $\text{CO}(\text{NH}\cdot\text{C}^6\text{H}_4\text{Cl})^2$, is obtained in long needles insoluble in the ordinary solvents, soluble without decomposition in strong sulphuric acid, partly subliming and decomposing at 270°, without previous fusion. (5). On leaving the alcoholic extract of the resinous mass to evaporate, and agitating the remaining liquid with ether, the hydriodide of tri-*p*-chlorophenyl-guanidine is precipitated as a white powder; and on leaving the ethereal filtrate to evaporate, and washing the residue with carbon disulphide, and filtering, the filtrate on standing deposits fine needles of triphenyl-guanidine, easily soluble in alcohol and ether, insoluble in water, resolved by heating to 230° with carbon disulphide into chlorophenyl-thiocarbamide and di-*p*-chlorophenyl-thiocarbamide (Beilstein a. Kurbatow).

Benzyl-thiocarbamide, $\text{NH}^2\cdot\text{CS}\cdot\text{NH}(\text{CH}^2\cdot\text{C}^6\text{H}_5)$, produced by the action of potassium thiocyanate on benzylamine hydrochloride, forms crystals soluble in water and in alcohol and melting at 101° (Paternò a. Spica, *Gazz. chim. ital.* v. 388).

Dibenzyl-thiocarbamide, $\text{NH}(\text{C}^6\text{H}_5)\cdot\text{CS}\cdot\text{NH}(\text{C}^6\text{H}_5)$, obtained by boiling an alcoholic solution of benzylamine with carbon disulphide, and recrystallising the residue left on evaporation, forms large shining four-sided plates, melting at 114°, insoluble in water, but soluble in alcohol and in ether (Strakosch, *Deut. Chem. Ges. Ber.* v. 692).

Isodibenzyl-thiocarbamide, $\text{NH}^2\cdot\text{CS}\cdot\text{N}(\text{C}^6\text{H}_5)^2$, prepared from potassium thiocyanate and dibenzylamine hydrochloride, forms large colourless needles moderately soluble in water, very soluble in alcohol and ether, melting at 150°–157° (Paternò a. Spica).

Paratolyl-thiocarbamide, $\text{NH}^2\cdot\text{CS}\cdot\text{NH}(\text{C}^6\text{H}_4\cdot\text{CH}^3)$ [$\text{NH} : \text{CH}^3 = 1 : 4$]. This compound is obtained in colourless plates, which melt at 188°, have a persistent bitter taste, and are nearly insoluble in water and in ether. They are decomposed by

CARBAMIDES (THIO-), ALCOHOLIC.

potash, with reproduction of paratoluidine (De Clermont a. Wehrlin, *Compt. rend.* lxxxiii. 347).

Ethyl-phenyl-thiocarbamide, $\text{CSN}^2\text{H}^2(\text{C}^2\text{H}^5)(\text{C}^6\text{H}^5)$. Hofmann (*Jahresb. f. Chem.* 1868, 666), described two modifications of this compound, one melting at 145° , obtained from ethyl-thiocarbamide and aniline, the other, melting at 97° , from phenyl-thiocarbamide and ethylamine. According to Weith, on the other hand, (*Deut. Chem. Ges. Ber.* viii. 1523), these two processes yield one and the same ethyl-phenyl-thiocarbamide, which forms large monoclinic crystals melting at 99° – 99.5° . When further heated, it begins to boil at 150° , giving off ethyl-thiocarbamide and ethylamine; and at 220° the thermometer remains stationary. Hydrogen sulphide escapes during the distillation, and the distillate is found to contain ethyl-phenyl-thiocarbamide and thiocarbamilide. When ethyl-phenyl-thiocarbamide is heated with aniline, ethylamine is given off, and thiocarbamilide is formed in large quantity (Weith).

Ethyl-phenyl-thiocarbamide, dissolved in benzene, is converted by boiling with lead oxide into carbethylphenylimide, $\text{C} \begin{smallmatrix} \text{N.C}^2\text{H}^5 \\ \text{N.C}^6\text{H}^5 \end{smallmatrix}$, which is reconverted by addition of SH^2 into ethyl-phenyl-thiocarbamide, and unites with aniline to form ethyldiphenyl-guanidine, $\text{C}^6\text{H}^5.\text{N}=\text{C} \begin{smallmatrix} \text{NH.C}^2\text{H}^5 \\ \text{NH.C}^6\text{H}^5 \end{smallmatrix}$ (Weith).

Allyl-phenyl-thiocarbamide or **Phenyl-thiosinamine**, $\text{CSN}^2\text{H}^2(\text{C}^3\text{H}^5)(\text{C}^6\text{H}^5)$, prepared from phenyl-thiocarbamide and allylamine, is identical with that which Zinin obtained from allyl-thiocarbimide (mustard-oil) and aniline (v. 783). It melts at 98° , and is resolved by hydrochloric acid into CO^2 , SH^2 , aniline and allylamine: hence it has the constitution $\text{NH}(\text{C}^3\text{H}^5).\text{CS.NH}(\text{C}^6\text{H}^5)$ (Weith).

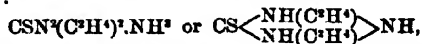
Ethyl-paratolyl-thiocarbamide, $\text{CSN}^2\text{H}^2(\text{C}^2\text{H}^5)(\text{C}^6\text{H}^4.\text{CH}^3)$, obtained either from paratolyl-thiocarbimide and ethylamine, or from ethyl-thiocarbimide and paratoluidine, crystallises in monoclinic plates melting at 96° – 96° (Weith).

Ditolyl-thiocarbamide, $\text{CSN}^2\text{H}^2(\text{C}^6\text{H}^4.\text{CH}^3)^2$, is formed, together with allyl-tolyl-thiocarbamide (tolyl-thiosinamine, 1st *Suppl.* 1089), by mixing an alcoholic solution of toluidine with mustard-oil. The two compounds are separated by warm alcohol, which easily dissolves the tolyl-thiosinamine, while the ditolyl-thiocarbamide remains behind, but may be dissolved by a large quantity of boiling alcohol, from which it crystallises in hard colourless granules melting at 176° . It is nearly insoluble in cold alcohol and in ether, dissolves with difficulty in hot benzene, and is insoluble in water. When heated, it melts, gives off vapours having a very strong odour of star-anise, and burning with a smoky flame. Small quantities of it heated in a glass tube sublime without residue in small fine crystals; with larger quantities partial decomposition takes place. It is insoluble in hydrochloric acid, even when hot and concentrated, also in potash and ammonia. Treated in hot alcoholic solution with silver nitrate, it yields silver sulphide and ditolyl-carbamide, $\text{CON}^2(\text{C}^6\text{H}^4)^2\text{H}^2$, melting at 263° (Maly, *Zeitschr. f. Chem.* [2], v. 258). For its other reactions, see 1st *Suppl.* 1051).

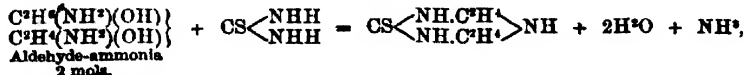
Naphthyl-thiocarbamide, $\text{NH}^2.\text{CS.NH}(\text{C}^{10}\text{H}^7)$, formed by heating naphthylamine hydrochloride with ammonium thiocyanate (1 mol. of each) on the water-bath for a few hours, crystallises in small rhombic prisms, which turn brown on exposure to the air, and melt at about 198° . It has a persistent bitter taste, dissolves sparingly in water, ether, and alcohol, more freely in boiling alcohol. Its alcoholic solution is desulphurised by lead oxide at the boiling heat. On adding a little nitrous acid to its solution in sulphuric acid, oxides of nitrogen are given off, and a brown flocculent substance is formed, possessing great tinctorial power (De Clermont a. Wehrlin, *Compt. rend.* lxxxii. 512).

B. Derivatives containing Diatomic Alcohol-radicles and Aldehyde-radicles.

Diethylidene-thiocarbamide, $\text{CSN}^2(\text{C}^2\text{H}^5)^2$, is obtained in the form of an ammonia compound:



by heating a moderately concentrated solution of thiocarbamide with aldehyde-ammonia:



its formation being analogous to that of ethylidene-carbamide by the action of thiocarbamide on aldehyde; $\text{C}^2\text{H}^5\text{O} + \text{CSN}^2\text{H}^2 = \text{CSN}^2\text{H}^2(\text{C}^2\text{H}^5) + \text{H}^2\text{O}$ (2nd *Suppl.* 1115).

The ammonia-compound is slightly soluble in boiling water, insoluble in cold alcohol and ether, and melts at 180° . Its aqueous solution, which is intensely bitter, is resolved by prolonged boiling, or more quickly in presence of acids, into aldehyde, thiocarbamide, and ammonia (Nencki, *Deut. Chem. Ges. Ber.* vii. 158).

Ethylidene-phenyl-oxethyl-thiocarbamide-ammonia, $C^6H^5N^3S^2O^2 = [CS \begin{smallmatrix} N(C^2H^5)(OC^2H^5) \\ N(C^2H^5) \end{smallmatrix}] NH^2 \cdot$ or $CS \begin{smallmatrix} N(C^2H^5)(OC^2H^5)(C^2H^5)(OC^2H^5)N \\ NH(C^2H^5) \end{smallmatrix} NH \begin{smallmatrix} (C^2H^5) \\ NH(C^2H^5) \end{smallmatrix}$ (R. Schiff, *Gazz. chim. ital.* vi. 244). This compound is formed by heating aldehyde-ammonia (2 mol.) in the water-bath with phenyl-thiocarbimide (1 mol.) dissolved in a moderate quantity of absolute alcohol. On cooling, the whole solidifies to a crystalline pulp, which may be purified by washing with cold alcohol and recrystallisation from boiling alcohol. The compound is thus obtained in white silvery needles having an intensely bitter taste, and melting at 148° . Chloroform is the only liquid which dissolves it readily at ordinary temperatures; at higher temperatures it dissolves abundantly also in alcohol, with moderate facility in water, sparingly in carbon disulphide, scarcely at all in ether or in benzene.

The formation of this compound, represented by the equation :



is analogous to that of diethylidene-thiocarbamide-ammonia by the action of aldehyde-ammonia on thiocarbamide: hence the compound itself may be represented by the constitutional formula above given.

This compound is not attacked by dilute acids in the cold, but when heated with them it gives off aldehyde. When hydrochloric acid gas is passed into its cooled solution in chloroform, a hydrochloride is thrown down in the form of a white jelly. Heated with strong hydrochloric acid to 150° , it yields aldehyde, hydrogen sulphide, carbon dioxide, ammonium chloride, and aniline. When added to warm *acetic anhydride*, it dissolves, with dark-red coloration, and emission of aldehyde, and as the liquid cools, acetyl-phenyl-thiocarbamide, $NH(C^6H^5).CS.NH(C^2H^5O)$, crystallises out (Schiff).

An analogous compound, $C^6H^5N^3S^2O^2$, containing allyl instead of phenyl, is formed from allyl-thiocarbamide (mustard-oil) and aldehyde-ammonia. It crystallises in white needles, melts without decomposition at 107° – 108° , dissolves readily in alcohol, chloroform, and hot water; less readily in cold water. It is altogether less stable than the phenyl-compound, and is decomposed even by boiling with dilute alcohol, more quickly with alkalis or acids, giving off aldehyde and ammonia. It forms, however, a hydrochloride which crystallises in microscopic needles. An attempt to recrystallise a considerable quantity of it from hot water resulted in its decomposition into ammonia, aldehyde, and thiosinamine (Schiff).

The corresponding ethyl-compound, $C^6H^5N^3S^2O^2$, obtained from aldehyde-ammonia and ethyl-thiocarbimide, is distinguished by its marked tendency to crystallise: it forms silvery needles melting at 118° – 119° , dissolves readily in alcohol, ether, chloroform, and hot water, less easily in cold water (Schiff).

Tolylene-dithiocarbamide, $C^6H^5N^3S^2 = NH^2.OS.NH.C^6H^5.NH.OS.NH^2$, is formed by molecular transposition of tolylenediamine thiocyanate, $N^2H^4(C^6H^5).C^2N^2S^2H^2$. When a warm concentrated aqueous solution of tolylenediamine sulphate is mixed with a warm solution of potassium thiocyanate, the liquid evaporated on the water-bath, the residue exhausted with alcohol, and the filtrate purified with animal charcoal, tolylenediamine thiocyanate is obtained in large transparent prisms easily soluble in water, and giving the reaction of the thiocyanates with ferric chloride. This salt, however, quickly changes, even without the aid of heat, into tolylene-dithiocarbamide, which is quite insoluble in water, whether hot or cold, and likewise in ether, and dissolves but very slightly in boiling alcohol; with moderate facility, however, in glacial acetic acid, from which water precipitates it as a white crystalline powder. It melts at 218° . Heated with phosphoric anhydride, or better with strong hydrochloric acid, it is resolved into ammonia and a thiocarbimide, $C^6H^5N^2S^2 = C^6H^5(NCS)^2$, which forms a brown transparent somewhat viscid oil, not volatile without decomposition (R. Lussay, *Deut. Chem. Ges. Ber.* vii. 1263; *viii.* 667).

Urbamide, $C^6H^5[NH.OS.NH(C^2H^5)]^2$, formed by with ethyl iodide, crystallises indistinctly and melts at 225° . The corresponding acetyl-compound, obtained in like manner with acetyl chloride, forms white needles melting at 232° , sparingly soluble in hot water, alcohol, and ether, moderately soluble in glacial acetic acid (Lussay).

$C^6H^5[NH.OS.NH(C^2H^5)]^2$ is formed on mixing the ethereal solutions of tolylenediamine and phenyl-thiocarbimide and

400 CARBAMIDES (THIO-) CONTAINING ACID RADICLES.

separates after a while as a white crystalline powder, melting at 238° . By heating with strong hydrochloric acid, it is resolved into the thiocarbamide above described, and tetraphenyl-guanidine, $\text{NH}=\text{C}[\text{N}(\text{C}^6\text{H}_5)]_2$, which separates in brown crystals (Lussy).

C. Derivatives containing Acid-radicles.

Acetyl-thiocarbamide, $\text{CS}(\text{C}^2\text{H}^3\text{O})\text{H}^1\text{N}^2 = \text{NH}^2.\text{CS}.\text{NH}(\text{C}^2\text{H}^3\text{O})$. Thiocarbamide dissolves easily in warm acetic anhydride, and the solution on cooling yields a yellow crystalline mass which, after several recrystallisations from hot water, yields colourless prisms of the acetyl-derivative. This compound dissolves easily in alcohol, less easily in ether, melts at 11.5° . The aqueous solution, which has a neutral reaction, gives with platinic chloride a crystalline, sparingly soluble double salt, $\text{CS}(\text{C}^2\text{H}^3\text{O})\text{H}^1\text{N}^2.2\text{HCl}.\text{PtCl}_4$ (Nencki, *Deut. Chem. Ges. Ber.* vi. 598).

Acetyl-thiocarbamide is also formed in small quantity when dry ammonia gas is slowly passed through an ethereal solution of acetyl thiocyanate, though the more usual product of this reaction is a compound of thiocyanic acid and acetamide, which separates as a yellow oil (Miguel, *Bull. Soc. Chim.* [2], xxv. 104).

Acetyl-phenyl-thiocarbamide, $\text{C}^6\text{H}^5\text{N}^2\text{OS} = \text{NH}(\text{C}^6\text{H}^5).\text{CS}.\text{NH}(\text{C}^2\text{H}^3\text{O})$, is formed, together with aldehyde, on adding the compound $\text{C}^{22}\text{H}^{31}\text{N}^2\text{S}^2\text{O}^2$ to warm acetic anhydride, and crystallises out on cooling (R. Schiff, p. 399).

It is also produced, similarly to acetyl-thiocarbamide, by the action of aniline on acetyl thiocyanate, the mixture being diluted with 2 or 3 vols. of ether, to moderate the reaction, which is otherwise very violent (Miguel). It crystallises in laminae having a nacreous lustre and splendid iridescence; melts at 173° (Schiff), at 168° – 169° (Miguel); dissolves easily in glacial acetic acid, ether, and chloroform, less easily in alcohol, and is nearly insoluble in water.

Benzoyl-thiocarbamide, $\text{CS} \begin{smallmatrix} \text{NH}^2 \\ \text{NH.CO.C}^6\text{H}^5 \end{smallmatrix}$, is formed: 1. By gently heating 1 mol. benzoyl chloride with 2 mols. thiocarbamide, whereby a yellow pasty mass is obtained, which solidifies at 120° (W. H. Pike, *Deut. Chem. Ges. Ber.* vi. 755). 2. By the action of aqueous ammonia on benzoyl thiocyanate, whereby ammonium-benzoyl thiocyanate, $\text{CN.S.C}^6\text{H}^5(\text{NH}^4)\text{O}$, is first produced, and then converted by molecular transposition into benzoyl-thiocarbamide (Miguel, *Bull. Soc. Chim.* [2], xxv. 252):



Benzoyl-thiocarbamide crystallises from alcohol in shining colourless needles melting at 169° – 170° (Pike); at 171° (Miguel). It has an intensely bitter taste, dissolves easily in ether and alcohol, sparingly in water (Pike), easily in alcohol, sparingly in hot water, also in ether and carbon disulphide (Miguel); forms a crystalline platinumchloride insoluble in water (Pike).

Benzoyl-phenyl-thiocarbamide, $\text{CS} \begin{smallmatrix} \text{NH.C}^6\text{H}^5 \\ \text{NH.CO.C}^6\text{H}^5 \end{smallmatrix}$, formed by the action of aniline on benzoyl thiocyanate, crystallises in silky flexible needles, melting at 149° , soluble in alcohol and ether, insoluble in water. It is decomposed by heating with nitric acid; but if the acid be added in large excess, and the liquid cooled after the thiocarbamide has dissolved, it deposits yellowish needles consisting of nitro-benzoyl-phenyl-thiocarbamide, $\text{CS} \begin{smallmatrix} \text{NH.C}^6\text{H}^5 \\ \text{NH.CO.C}^6\text{H}^5\text{NO}^2 \end{smallmatrix}$. This compound melts at about 30° , dissolves sparingly in alcohol and ether, and volatilises when heated on platinum foil.

Benzoyl-phenyl-thiocarbamide is resolved by prolonged boiling with acids, into benzonitrile, carbon dioxide, and hydrogen sulphide (Miguel).

Benzoyl-benzyl-thiocarbamide, $\text{CS} \begin{smallmatrix} \text{NH.CH}^2\text{C}^6\text{H}^5 \\ \text{NH.CO.C}^6\text{H}^5 \end{smallmatrix}$, from benzylamine and benzoyl thiocyanate, forms small prisms soluble in alcohol and ether, insoluble in water, melting at 145° , and afterwards solidifying to a plastic mass (Miguel).

Glycolyl-thiocarbamide or Thiohydantoin, $\text{C}^2\text{H}^4\text{N}^2\text{OS} = \text{CS} \begin{smallmatrix} \text{NH.CH}^2 \\ \text{NH.CO} \end{smallmatrix}$ (Volhard, *Liebigs Annalen*, clxvii. 383; Maly, *ibid.* clxviii. 133, 138). The hydrochloride of this base, isomeric with chloracetyl-thiocarbamide, $\text{NH}^2.\text{CS}.\text{NH}(\text{C}^2\text{H}^3\text{ClO})$, is produced, with violent reaction, on gently heating a mixture of monochloroacetic acid and thiocarbamide in molecular proportion:



This hydrochloride is easily soluble in water, sparingly in alcohol, almost insoluble

in ether. From its aqueous solution it separates on slow cooling or evaporation in well-defined prisms. It forms a platinochloride, $2(C^6H^5N^2OS.HCl).PtCl_4$, which crystallises in specular laminae, and a crystalline aurochloride. It is decomposed by sulphuric acid at ordinary temperatures, with effervescence and evolution of hydrochloric acid, and on adding nitric acid and silver nitrate to its aqueous solution, the whole of the chlorine is precipitated in the form of silver chloride. These reactions show that the compound in question cannot have the constitution of chloroacetyl-thiocarbamide. The aqueous solution of the hydrochloride is not precipitated by lead acetate; but on adding potash and boiling, a precipitate of lead sulphide is slowly formed. Mercuric chloride acts in a similar manner; mercuric oxide does not separate the sulphur even on boiling.

Caustic alkalis or alkaline carbonates added at ordinary temperatures to the aqueous solution remove the chlorine, and throw down glycolyl-thiocarbamide, $C^2H^2N^2OS$, which crystallises from hot water or dilute alcohol in long shining needles, and is reconverted into the hydrochloride by solution in hydrochloric acid.

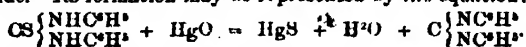
Glycolyl-thiocarbamide is readily soluble in hot, sparingly in cold water, nearly insoluble in alcohol and ether, and decomposes when melted. It is not desulphurised by boiling its aqueous solution with oxide of lead or mercury; it is slowly desulphurised by iodine, easily by bromine, very easily by mercuric oxide in presence of ammonia.

CARBETHYL-PHENYLIMIDE, $C^6H^5N^2 = (C^6H^5)N = C = N(C^2H^3)$, is formed by desulphuration of ethyl-phenyl-thiocarbamide dissolved in boiling benzene by means of pulverised lead oxide. It is reconverted into ethyl-phenyl-thiocarbamide by addition of H^2S , and converted, by addition of aniline, into ethyldiphenyl-guanidine, $C^6H^5 - N = C < \begin{smallmatrix} NH.C^6H^5 \\ NH.C^6H^5 \end{smallmatrix}$ (Weith, *Deut. Chem. Ges. Ber.* viii. 1630).

IDM, $C^{11}H^{11}NO = C^6H^5(C^2H^3)(CH^3)(CONH^2)$, is obtained by distilling potassium cymonesulphonate, $C^6H^{11}SO^2K$, with potassium cyanide, and saponifying the solid portion of the distillate (impure cymyl-cyanide, $C^6H^{11}.CN$) with alcoholic potash. It forms white needles, melting at $188^\circ - 139^\circ$, slightly soluble in cold water, easily soluble in alcohol, ether, and chloroform (Paternò & Fileti, *Gazz. chim. ital.* v. 30).

CARBODIIMIDE or **CARDIIMIDE**. Names given by E. Mulder to cyanamide, which he represents by the formula $C(NH)^2$ (2nd Suppl. 404).

CARBODIPHENYLIMIDE, $C^{12}H^{10}N^2 = C(NC^6H^5)^2$ (Weith, *Deut. Chem. Ges. Ber.* vii. 10, 1303). When thiocarbamilide dissolved in hot benzene is digested with mercuric oxide, an energetic reaction sets in, and the liquid on cooling deposits a small quantity of a crystalline body having the melting point and reactions of carbamilide. On evaporating the benzene, a colourless syrup remains, which gradually solidifies into a vitreous mass. This compound is carbodiphenylimide, isomeric with diphenylecyanide. Its formation may be represented by the equation:



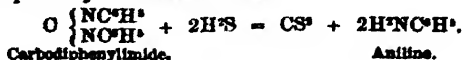
It changes spontaneously into an opaque porcelain-like mass, which gradually becomes crystalline, and is probably polymeric with the vitreous form. It melts at $168^\circ - 170^\circ$. When heated it evolves a pungent vapour, which, when much diluted with air, smells like cinnamon. Hydrochloric acid passed into a solution of carbodiphenylimide in benzene throws down a crystalline precipitate of the hydrochloride, $C^{12}H^{10}N^2.HCl$.

Carbodiphenylimide unites very readily with the elements of water, yielding diphenyl-carbamide. This transformation may be effected by the action of alcohol upon the hydrochloride, by treating the same compound with weak solution of soda, or even by boiling pure carbodiphenylimide with spirit of wine.

Carbodiphenylimide combines directly with aniline, producing α -triphenyl-guanidine, and with ammonia, probably forming diphenyl-guanidine.

When carbodiphenylimide is heated to about 170° in hydrogen sulphide, carbon disulphide is evolved. The residue consists of α -triphenyl-guanidine, thiocarbamilide, and aniline.

The reaction probably occurs as follows:—



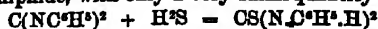
The α -triphenyl-guanidine which is formed results from the union of carbodiphenylimide with a portion of the aniline.

When hydrogen sulphide is passed into a cold solution of carbodiphenylimide in

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benzene, the only product formed is thiocarbamide, $\text{CS}(\text{NH}.\text{C}^{\text{H}}\text{H}^{\text{H}})^2$; and this, when heated to 160° - 170° with hydrogen sulphide, is almost completely resolved into aniline and carbon disulphide, with only a very small quantity of triphenyl-guanidine:



and $\text{CS}(\text{N}.\text{C}^{\text{H}}\text{H}^{\text{H}}.\text{H})^2 + \text{H}^2\text{S} = \text{CS}^2 + 2(\text{NH}^2.\text{C}^{\text{H}}\text{H}^{\text{H}}).$

When carbodiphenylimide and diphenyl-carbamide are heated together, they begin to react below 150° , and at higher temperatures phenyl cyanate distils over, and the residue of the distillation contains α -triphenyl-guanidine. With the hydrochloride of carbodiphenylimide, the action begins at 140° , and is complete after an hour's heating. The phenyl cyanate thus obtained unites with ammonia to form monophenyl-carbamide (p. 390).

phenyl-thiocarbimide acts upon carbodiphenylimide even at 100° , but more at 150° , forming α -triphenyl-guanidine and phenyl-thiocarbimide. The action takes place more quickly when a solution of carbodiphenylimide (1 mol.) in benzene is mixed with diphenyl-thiocarbamide (1 mol.) and hydrochloric acid (1 mol.), or hydriodic acid (1 mol.) dissolved in alcohol, and the mixture is heated for a few minutes on the water-bath.

When a mixture of diparatolylthiocarbamide, hydrochloric acid, and carbodiphenylimide is heated with alcohol for about an hour, paratolyl-phenyl-thiocarbimide and the hydrochloride of a tolylphenyl-guanidine are formed, together with small quantities of phenyl-thiocarbimide (Weith, *Deut. Chem. Ges. Ber.* ix. 810).

Carbodiphenylimide Hydrochloride is obtained by passing hydrogen chloride into a moderately strong solution of carbodiphenylimide in benzene, till the white crystalline precipitate at first produced is redissolved. On cooling, the hydrochloride crystallises in needles having a strong lustre (Weith).

CARBOHYDROQUINONIC ACID, syn. with **PROTocatechuic acid**. See **BENZOIC ACIDS** (DIOXY-), p. 289.

CARBON. 1. *Diamond*.—The following determinations of the specific gravity of diamonds (compared with water at $+4^{\circ}$, and reduced to a vacuum) have been made by E. H. v. Baumhauer (*Archives néerlandaises*, viii. 1).

	Sp. gr.
Brilliant, nearly colourless, from the Cape	3.51812
Brilliant, faintly yellow, from the Cape	3.52063
Rough diamond, yellowish, from the Cape	3.51727
Rough diamond, small, perfectly clear, from the Cape	3.51631
Rough diamond, with a small black speck in the interior, from the Cape	3.51934
Rough diamond, with large speck and cracks, from the Cape	3.50307
Rough diamond, clear, formed of two crystals, from the Cape	3.51436
Bord, spheroidal, grey, translucent, but not transparent	3.50383
Bord, spheroidal, white, from the Cape	3.50329
Bord, small, from the Cape	3.49806
Grey carbonado, from Brazil	3.20053
Grey-black carbonado, from Brazil	3.20287
Black carbonado, from Brazil	3.15135
Spheroidal carbonado, from Brazil	3.44497
Spheroidal carbonado, from Brazil	3.20378
Grey mass, semitranslucent, distinctly crystalline	3.50652
White mass, semitranslucent, slightly crystalline	3.50216

The mean density of the first five of these stones is 3.51835 at 4° . The number 3.51432, found by R. v. Schrötter (*Jahresbericht*, 1871, 257) as the mean of a large number of determinations, is regarded by v. Baumhauer as too low.

Effect of High Temperatures on the Diamond.—Diamonds heated to whiteness in a platinum crucible exhibited no diminution of specific gravity, lustre, or transparency. A light green diamond acquired by ignition a yellowish, a dark-green diamond a violet colour, without alteration of weight in either case. Brown diamonds became by ignition more or less grey, and considerably more transparent; and when subsequently examined by the microscope, they appeared perfectly clear but beset with small black specks. Yellow diamonds, like most of those from the Cape, and grey diamonds underwent no change of colour (v. Baumhauer, *loc. cit.*)

The incomplete combustion of the diamond in oxygen gas was never observed to be attended with blackening or splitting, so that transformation into coke or graphite under these circumstances appears doubtful. During the combustion, the diamond was enveloped in a bluish-violet flame, like that of burning carbonic oxide (v. Baumhauer).

Diamonds heated to whiteness in a stream of aqueous vapour undergo no

alteration whatever; but in a stream of carbon dioxide they lose weight and become dull (v. Baumhauer). This last change was previously observed by Jaquelain (*Ann. Chim. Phys.* [3], xx. 468).

The behaviour of the diamond at high temperatures has also been examined by G. Rose (*Pogg. Ann.* cxlviii. 497). The diamond was first ignited in a vacuum by means of a powerful electrodynamic apparatus, being placed between carbon poles and resting on one of them. It split into fragments as soon as a red heat had been reached. A second experiment was made with the same result. The diamond was partially changed to graphite on the surface, as the heat had probably been applied too suddenly. A third experiment was made, in which the diamond was placed in a hole bored in a small cube of the hard carbon which deposits in gas retorts, and this cube was placed in a graphite crucible filled with wood-charcoal, and heated for half an hour to the melting-point of cast-iron. The diamond suffered no change. A second experiment was made with a rosette-cut diamond, but, with this difference, that the heat was applied only for ten minutes. On examination, the surface was found to be opaque and black, with a bright metallic lustre. This crust was confined to the surface, for on breaking the diamond, the interior was unchanged.

R. v. Schrötter, who made similar experiments, found that on one occasion the surface of the diamond had become dull; and a diamond wrapped in platinum foil was blackened, with black streaks running through the interior, while the foil was fused to a button.

The diamond, when heated in a muffle through which a current of air is passing, grows smaller and smaller, keeping its brilliancy till it finally disappears, and emitting a faint light at the last moment. The octohedral and cleavage surfaces become indented with microscopic triangular impressions, which resemble those formed when a crystal is attacked by an acid. The edges are in no case rounded off in burning; each atom goes at once from the solid into the gaseous state. The diamond shows no sign of changing to graphite during combustion, but sometimes becomes opaque. A small splinter may even be burnt before the blowpipe; it does not blacken. Fourcroy, in 1782, on exposing diamonds to a high temperature in a muffle, found that they became covered with a black coating. Rose explains this by supposing that, as the older form of muffles had side openings, the smoke from the furnace might have coated the diamonds. However, all accounts of experiments in which diamonds have been exposed in the focus of a concave mirror, describe them as becoming black; and the same occurs, as already observed, in the oxyhydrogen flame.

Some diamonds are naturally black. This appears to be a pseudomorphosis of graphite into diamond, but is possibly produced on the diamond by heat. A black diamond heated in melting saltpetre, underwent no change, showing that the blackness was due to graphite, not to amorphous charcoal.

A variety of diamond called 'Carbonado,' or 'Carbonate,' is found in the Soap Mountains of Bahia. Pieces of this substance are said to have been found from one to two pounds in weight. A specimen in the Berlin Museum has no lustre, but appears porous when examined with a lens; its colour is reddish-grey, and four pieces of carbonado exhibited a sp. gr. of 3.012, 3.341, 3.416, and 3.255 respectively, which is obviously that of the diamond. Carbonado heated to whiteness in a muffle gave off small bubbles, losing its sharply cut edges, and becoming more porous; also its surface grew dull. Söppert ascribes the formation of bubbles to the carbonic anhydride which escapes, but nothing similar to this occurs in the combustion of the diamond; it may be assumed, therefore, to be due to air escaping. Rivot found in three specimens of carbonado, 2.03, 0.24 and 0.27 per cent. of ash, consisting probably of alumina coloured by iron. Carbonado may be used for polishing diamonds, and for boring machines. Only three specimens of carbonado are known which possess a crystalline form; whether they are true crystals or not is a matter of doubt.

2. *Graphite*.—To obtain pure graphite, the native substance must be very finely pulverised and repeatedly treated with alkali, aqua regia, and hydrofluoric acid. The amount of ash may thus be reduced to 0.12 per cent., and in the case of graphite from Bohemia and Styria still further. Sometimes the ferric oxide present in graphite exists in the soluble state, and sometimes in the insoluble state, and the graphite from Styria frequently contains fragments of easily pulverisable quartz. In purifying graphite an effectual elutriation is of great importance.

When graphite from Bohemia or Styria is carefully purified and converted into graphitic acid (ii. 941), the product forms a yellow amorphous powder, no crystalline structure being visible; and when this graphitic acid is heated, a residue is obtained which decolorises, and possesses a covering power greater than that of lamp-black. Foliated or crystalline graphite yields, on the other hand, a graphitic acid which is crystalline, and the residue obtained by heating it possesses neither decolorising nor covering power. The graphite from crude soda-ley (from the Aussig works)

was found to contain 79.79 per cent. of carbon, 11.27 per cent. of ferric oxide, and 10.05 per cent. of silica. The presence of ferric oxide in this kind of graphite tends to show that the sodium cyanide and sodium ferrocyanide contained in the crude soda are converted by oxidation into carbon monoxide, nitrogen, magnetic oxide of iron and sodium hydrate, and that the action of carbon monoxide on magnetic oxide of iron gives rise to the formation of ferric oxide and graphite (*J. Stingl, Deut. Chem. Ges. Ber. vi. 391*).

Behaviour at High Temperatures.—The purer varieties of natural graphite often sustain on ignition a loss of weight which is considerable in comparison with the earthy residue left. The following results bearing on this point have been obtained by Rammelsberg (*ibid. vi. 187*):

	Loss on ignition.	Earthy matter.
Ticonderoga, New York	3.85 per cent.	
Ceylon II	2.56 "	1.28 per cent.
Borrowdale	3.8—5.08 "	7.0 "
Oberer Jenisei (Alibert).	2.53 "	4.5 "
Tunguska (Sidorow)	1.77—2.38 "	6.53 "

After fusion with caustic soda, digestion with acids, washing, and drying, inorganic matter is still left on combustion.

Ticonderoga	0.24 per cent.
Oberer Jenisei	0.60 "
Arendal	0.64 "

Some varieties of graphite burn on fused nitre, others do not. To the first class belong samples from Ceylon (I), Borrowdale, Oberer Jenisei, Upernivik (Greenland), and Arendal; the sp. gr. of these varies from 2.257 to 2.321. To the second class belong Ceylon (II), Ticonderoga, and graphite from blast-furnaces, in which the sp. gr. varies from 2.17 to 2.30.

Carbon of White Pig-Iron.—The carbonaceous residue left after treating white pig-iron with solution of copper sulphate, washing the carbonaceous copper, and then treating it with ferric chloride and hydrochloric acid, is a brownish, pulverulent substance, which, after washing with hydrochloric acid and water, and drying at 100°, gave on analysis in 100 parts:

Carbon.	Water.	Siliceous ash.	Not determined.
64.00	26.10	8.1	1.8

The weight of the combined carbon was found to be 63.1 per cent. of the residue; that of the graphite 1.2 per cent. The residue, after deducting the silicon and impurities, consists of a hydrate of carbon, exhibiting the ratio $11C : 3H_2O$. This ratio of carbon and water is constant for the products yielded by various white pig-irons, and is moreover the same as in the iodised hydrate (59.69 per cent. carbon, 22.50 water, and 16.0 iodine), which Eggertz obtained by the action of water and iodine on metallic iron; it connects this body, as graphitic hydrate, with Brodie's graphitic acid series, and with Berthelot's graphitic oxide.

This hydrate of carbon, heated to 250°, rapidly loses water. Ordinary nitric acid attacks it when heated, and transforms it into a red-brown amorphous body, soluble in excess of the acid, in alcohol, fixed alkalis, ammonia, and water, from which solution neutral salts precipitate it. Heated in a tube, it emits a distinct hydrocyanic odour; the residue was reconverted into the red-brown substance by nitric acid. It gave on analysis, 52.13, 52.41 per cent. carbon, 3.47–3.58 hydrogen, and 2.76 nitrogen, leading to the formula $C^2H^{17}(NO^2)O^{11}$, or $Gr^2H^{17}(NO^2)O^{11}$. This substance, which is called nitro-graphitic acid, is supposed to be identical with the product yielded by pig-iron on treatment with nitric acid (Schützenberger & Bourgoois, *Compt. rend. lxxx. 911*).

CARBON IODIDE, CI_4 . This compound is formed by mixing carbon tetrachloride, diluted with an equal volume of carbon bisulphide, with a saturated solution of aluminium iodide in carbon sulphide. It crystallises in regular octohedrons, having a red colour and a sp. gr. of 4.32 at 20.2°. Air decomposes it slowly at the ordinary temperature, but more rapidly at 100°, into carbonic anhydride and free iodine. It dissolves in carbon disulphide, alcohol, ether, and methyl iodide, and when in solution is very easily decomposed by air. Boiled with water or weak hydriodic acid, it yields iodoform. Alcoholic solution of potash decomposes it easily, but neither aqueous potash nor sulphuric acid acts on it rapidly (Gustavson, *Compt. rend. lxxviii. 382*).

CARBON OXIDES, Suboxides. Berthelot (*Bull. Soc. Chim. [2], xxi. 102*) has obtained a suboxide of carbon, $C^2O^2(?)$, apparently identical with that described by Brodie (2nd Suppl. 259), by the action of the galvanic current on carbon monoxide.

It is a brown amorphous substance, having the consistence of an extract, and somewhat resembling the brown acids which are obtained by oxidation in the wet way from various forms of carbon. It is very soluble in water and alcohol, insoluble in ether; has an acid reaction; gives brown precipitates with silver nitrate, lead acetate, and baryta-water. Heated to 300° – 400° in an atmosphere of nitrogen, it decomposes, yielding equal volumes of CO and CO^2 , and another darker-coloured oxide, C^2O^2 , which at a higher temperature suffers further decomposition, leaving a charcoal still containing oxygen. This gradual progress of the decomposition resembles that which takes place in the decomposition of hydrocarbons by heat.

Monoxide, CO. Lorin (*Compt. rend.* lxxxii. 750) has observed the formation of this gas under the following circumstances. Dehydrated oxalic acid heated in an oil-bath is resolved into water and equal volumes of CO and CO^2 . These two gases are also obtained when oxalic acid is heated with concentrated formic acid, but in this case the monoxide is in excess. This gas is likewise evolved when dehydrated alkaline formates and acetates are heated with formic acid, an acid salt being formed in the first instance, which at a higher temperature gives off carbon monoxide, leaving a neutral salt which remains unaltered. The action of dehydrated oxalic acid and of alkaline acetates and formates on formic acid is therefore exactly analogous to that of strong sulphuric acid.

On the formation of Carbon Monoxide in the Blast Furnace, see 2nd Suppl. p. 703; also *Chem. Soc. J.* 1873, pp. 667, 677.

Carbon monoxide is rapidly absorbed by anhydrous hydrocyanic acid cooled by a freezing mixture. On adding strong hydrochloric acid, the two liquids do not mix, but form separate layers; and on removing the tube from the freezing mixture a steady evolution of carbon monoxide takes place, becoming violent on gentle heating. No glyoxylic acid is formed, as might have been expected according to the equation, $\text{CNH} + \text{CO} + 2\text{H}^2\text{O} = \text{NH}^2 + \text{C}^2\text{H}^2\text{O}^2$ (Böttinger, *Deut. Chem. Ges. Ber.* x. 1122).

Carbon monoxide is not oxidised by ozone, either in diffused daylight or in direct sunshine (Remsen & Southworth, *Sill. Amer. J.* [3], xi. 136). This result is somewhat remarkable, inasmuch as Ludwig has found that the oxidation of CO to CO^2 takes place under the influence of nascent oxygen from chromic acid (2nd Suppl. 350).

On the formation of Propionic acid from carbon monoxide, see PROPIONIC ACID.

Dioxide, CO^2 . *Occurrence in Air and Water.*—The observations of Weend and of Pittbogen & Hasselbarth on the average amount of this gas in the atmosphere, and those of Truchot on the variations of its amount in the air of Auvergne at different seasons and at different heights, are given under ATMOSPHERE (p. 132).

The results of daily observations of the amount of carbon dioxide in the air, made in 1874–75 at Tabor in Bohemia, have been published by F. Farský (*Wien. Akad. Ber.* [2 Abth.], lxxiv. 67).

Muir (*Chem. News*, xxxiii. 16) has determined the amount in the air of several places on the sea-coast, and found that it agrees with that of inland localities. Thorpe, on the other hand, found that the amount of this gas in sea-air is considerably less than that in air over the land (1st Suppl. 232).

CO^2 in the Air of Rooms.—From a considerable number of determinations by E. Schulze (*Arch. Pharm.* [3], ix. 412), it appears that the maximum amount of this gas consistent with a healthy state of the air of inhabited rooms, as determined by Pottenkofer (*Chem. Soc. J.* x. 292), viz. 9 to 10 c.c. CO^2 in 10 litres of air, is generally exceeded even under the most favourable conditions. Schulze is therefore of opinion that this limit has been fixed too low.

Amount of Carbon Dioxide in Sea-water.—From observations by O. Jacobsen, (*Deut. Chem. Ges. Ber.* ix. 1793), it appears that sea-water contains very large quantities of carbon dioxide, which are not completely expelled by passing indifferent gases through the water, or by heating it, even in a vacuum. Jacobsen attributes the retention of the carbon dioxide to the simultaneous presence of magnesium chloride and calcium carbonate in the water, inasmuch as an artificially prepared mixture of these two salts does not deposit any calcium carbonate when boiled, but retains the carbonic acid. Nevertheless, the absorption-coefficient of a solution of magnesium chloride for carbon dioxide is not greater than that of pure water, though when such a solution is charged with carbon dioxide under pressure, it gives off the excess of that gas but slowly.

Absorption by Saline Solutions.—Satschenow (*Deut. Chem. Ges. Ber.* vi. 1461) has made observations on the absorption of carbon dioxide by solutions of alum, $\text{K}^2\text{Al}(\text{SO}^4)^2 + 24\text{H}^2\text{O}$, magnesium sulphate, $\text{MgSO}^4 + 7\text{H}^2\text{O}$, and zinc sulphate, $\text{ZnSO}^4 + 7\text{H}^2\text{O}$, from which he deduces the following simple laws: The solutions of these salts are absorptiometrically equivalent, when they contain equal percentages of crystallisation-water. Hence in solutions containing equal quantities of salt, the

magnesium salt⁸ hinders the absorption of carbon dioxide to the greatest extent, then the zinc salt, and lastly the aluminium salt. The law may also be expressed as follows: *In salts of similar structure and equal amount of crystallisation-water, the chemical equivalents are likewise the absorptiometric equivalents.*

Absorption by Sodium Salts.—These salts, with regard to their capacity of absorbing carbon dioxide, may be divided into two groups, viz.: (1). Those which do not combine with carbon dioxide, such as common salt. A solution of these absorbs the gas according to Dalton's law, and the more concentrated the solution, the less gas is dissolved. (2). Salts which combine chemically, such as the carbonate, phosphate, borate, and neutral citrate. With these, the more concentrated the solution, the more carbon dioxide is absorbed, but the quantity does not increase proportionally to the pressure. The neutral oxalate stands between the two groups, inasmuch as the quantity of gas which it absorbs does not depend on the concentration of the solution (Setschenow, *ibid.* viii. 694).

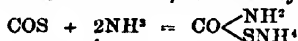
1 mol. disodic phosphate, Na_2HPO_4 , in dilute solution, absorbs 2 mols. CO_2 ; at the same time a chemical action takes place, resulting in the formation of NaH_2PO_4 and NaHCO_3 (Setschenow, *Chem. Centr.* 1875, 97).

According to Horsford (*Chem. Centr.* 1873, 370), when sodium phosphate and ferrous phosphate are placed together in an atmosphere of carbon dioxide, this compound is reduced, either in light or in darkness, to monoxide.

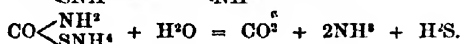
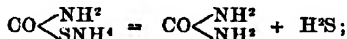
CARBON OXYSULPHIDE, COS. This compound is formed, together with others, when a mixture of the vapours of carbon disulphide and alcohol is passed over red-hot copper (p. 407).

Reaction with Ammonia.—When carbon oxysulphide is passed into strong aqueous ammonia, it is largely absorbed, the solution acquiring a faint yellow colour. On evaporating the still strongly alkaline liquid in glass basins, ammonium carbonate and hydrogen sulphide escape and urea is left in crystals.

This formation of urea, &c., is preceded by that of ammonium oxythiocarbamate: for when carbon oxysulphide is passed into aqueous ammonia cooled to 0° , the solution gives at first no precipitate with baryta-water, and no coloration with lead paper; but after a time both these reactions occur. Hence it appears that 1 mol. of carbon oxysulphide unites with 2 mols. of ammonia, as shown by the equation:



and that the ammonium oxythiocarbamate thus formed breaks up in the following ways:—



The former of these decompositions takes place almost exclusively when ammonia saturated with carbon oxysulphide in the cold is at once agitated with hydrate or carbonate of lead, so that, on evaporating the filtrate, a considerable quantity of urea is left behind (Ernst Schmidt, *Deut. Chem. Ges. Ber.* x. 191).

CARBON SULPHIDES.—1. **Monosulphide, CS.** This compound, discovered by Sidot (*Compt. rend.* lxxxi. 32), is formed as a brown precipitate when the disulphide is exposed to sunshine: it may be purified by distilling off the undecomposed disulphide, washing the residual mixture of sulphur and monosulphide with pure carbon disulphide till the free sulphur is removed, and then drying it at 150° in a current of hydrogen gas (Sidot). It may also be prepared by leaving the crude disulphide in contact with a few pieces of pure iron wire in a test-tube for about six weeks, by which time the whole of the disulphide will have disappeared, being converted into a reddish-brown solid substance, consisting of a mixture of iron disulphide and carbon monosulphide, formed according to the equation $2\text{CS}_2 + \text{Fe} = \text{FeS}_2 + 2\text{CS}$. By treating this substance with hydrochloric acid, which dissolves the iron sulphide, the carbon monosulphide may be obtained pure.

Carbon monosulphide is a maroon-red powder, having neither smell nor taste. gr. = 1.66. It is insoluble in water, alcohol, turpentine-oil, and benzene; soluble in carbon disulphide and in ether at the boiling point of these. Boiling nitric acid dissolves it. When the monosulphide and concentrated nitric acid come in contact, the sulphide is immediately ignited. Hydrochloric and sulphuric acids do not attack the monosulphide. Concentrated boiling sulphuric acid dissolves it; it is reprecipitated from this solution by acidifying. Towards water the monosulphide splits up into its elements, a little disulphide being also formed. On heating it with excess of sulphur it is converted into the disulphide.

A red substance, perhaps consisting of carbon monosulphide, has been observed by L. Thomson (*Chem. News*, xlv. 84), in the ammoniacal liquor of gas-works.

Disulphide or Bisulphide, CS₂. *Purification.*—When carbon disulphide, purified by distilling it off palm oil (which is recommended as the most convenient means of purification on the large scale), is agitated with red fuming nitric acid, it takes up the vapour of nitrogen tetroxide, both liquids acquiring the same colour. The disulphide, when separated and filtered, fumes in moist air and remains unaltered for weeks. On adding cold water to a mixture of disulphide and fuming nitric acid, the disulphide assumes a rose-red to violet colour, and when washed with water turns milky, but after filtering it forms a clear violet liquid, more highly refractive than the ordinary disulphide. When this liquid is carefully distilled between 60° and 60°, carbon disulphide goes over, leaving the colouring matter behind. The distillate, after washing with water and re-distillation, is chemically pure. The colouring matter, which has as yet been obtained in very small quantity only, is solid, brown, acid, and easily decomposable. The violet coloration is produced equally in carbon disulphide which has been previously purified by fuming nitric acid, on again treating it with that acid and water. It is not produced by washing with water the brown solution of nitrogen tetroxide acid in the disulphide, or by passing nitrous anhydride into the disulphide, the liquid in the latter case acquiring the well-known bluish-green colour of nitrous anhydride (Friedburg, *Deut. Chem. Ges. Ber.* viii. 1616).

According to Marquart (*ibid.* ix. 127), the violet coloration observed by Friedburg is due to iodine, which is almost always present in commercial nitric acid.

Solidification.—Drying oils, such as boiled linseed oil, when treated with a small quantity (10 per cent.) of sulphur chloride, solidify to a transparent elastic substance containing sulphur; and if carbon disulphide be added at the moment of solidification, a gelatinous mass is formed containing 10 per cent. of disulphide. The jelly thus formed does not melt at 100°, is difficult to ignite, and gradually gives off the carbon disulphide on standing. The vapour-tension of this compound is 218 mm. at 10°, and the mercury falls slowly; with pure carbon disulphide the mercury falls at once to 282 mm. (Mercier, *Compt. rend.* lxxiv. 916).

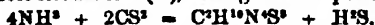
Reactions.—1. When nitrogen monoxide is passed over pumice-stone moistened with carbon disulphide, a gaseous mixture is produced, which burns with a flame very rich in chemical rays. If burned in a lamp having a Bunsen burner, and so constructed as to prevent explosion, it produces a flame superior in actinic power to that of magnesium (Delachanal a. Mermet, *Compt. rend.* lxxix. 1078).

2. When a mixture of the vapours of carbon disulphide and alcohol is gradually passed over red-hot copper, a gaseous mixture is produced, consisting of carbon oxysulphide, methane, ethane, acetylene, and aldehyde, while the copper is converted into sulphide. All the volatile products, except carbon oxysulphide and acetylene, are obtained when alcohol-vapour alone is passed through a red-hot tube. The formation of carbon oxysulphide may be represented by the equation:



the ethane C₂H₆ being further resolved into CH₄, C₂H₄, &c. (Carnolley, *Chem. Soc. J.* 1876, 523).

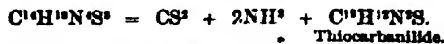
3. With Ammonia and Aniline.—According to Hlasiwetz (*Chem. Centr.* 1872, 632) carbon disulphide forms with ammonia (in presence of a third body, which is itself unchanged) a crystalline colourless solid (A), having the composition C²H¹⁰N⁴S², thus:—



and yielding, with weak oxidising agents, a solid crystalline body (B), having the composition C²H¹⁰N⁴S², insoluble in cold water, but decomposed by boiling water into carbon sulphide, ammonium thiocyanate, and free sulphur:

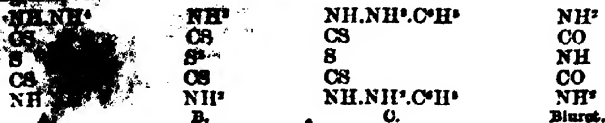


Aniline yields, by the action of carbon sulphide, the corresponding salt (C), which has the composition C¹⁰H¹⁰N⁴S², and is decomposed by boiling with water according to the equation:



Thiocarbamide.

The relation of these three substances to one another, and to biuret, is shown by the following formulae:



Detection of Carbon Disulphide in Mustard-oil.—The method consists in distilling off the carbon sulphide and treating it with alcoholic potash and cupric sulphate, whereby cuprous xanthate is produced. A small flask is fitted with a cork, through which passes a small test-tube, and also a piece of narrow glass tubing similar in shape to the blowing-tube of a wash-bottle. The test-tube is also fitted with a cork, through which passes a glass tube, bent downwards and drawn out at its lower end to a point; this end passes through a cork into another test-tube. Water is placed in the flask, and the oil to be tested in the small test-tube. At the temperature of boiling water any carbon disulphide distils over into the receiver, to which a drop of water has been previously added. On absorbing this water by means of blotting paper, adding $\frac{1}{2}$ –1 c.c. of a solution of caustic potash in absolute alcohol, acidulating after a short time with a drop of acetic acid, and adding a drop of copper sulphate solution, a lemon-coloured precipitate (cuprous xanthate) is produced. If the quantity of carbon disulphide is very small, only a few oily drops form in the tube connecting the two pieces of the apparatus. These must be washed into the receiving tube with caustic potash in alcohol, and the solution tested as above (E. Luck, *Zeitschr. anal. Chem.* xi. 410).

Estimation of Carbon Disulphide in Commercial Alkaline Thiocarbonates.—The following method is founded on the decomposition of lead thiocarbonate by boiling with water into lead sulphide and carbon disulphide, and the extreme solubility of the latter in olive-oil: 10 grams of the alkaline thiocarbonate are placed in a 500 c.c. flask with about 150 c.c. of water, and about 160 c.c. of a 10 per cent. solution of lead acetate are added gradually whilst the contents of the flask are kept agitated; to the precipitate, 10 c.c. of acetic acid of 8 degrees are then added. The flask is closed with a cork pierced with two holes, through one of which passes a safety-funnel, and through the other a delivery-tube leading to a washing-flask containing sulphuric acid, which is connected, by india-rubber tubing, with a second about three-quarters filled with olive-oil. This latter is carefully weighed. The contents of the large flask are then heated to boiling, the temperature of the sulphuric acid in the washing flask being also raised to about 120°. After about ten minutes' boiling, the flask is detached, an aspirator being connected with the washing-flask containing the olive-oil, and air is drawn slowly through for a few seconds, during which time the glass tube of the oil-flask is carefully warmed, and any drops of carbon disulphide that may have condensed therein, tilted into the body of the flask, which is then weighed. The error is never greater than 0.5 per cent., when the experiment is carefully conducted. Scientific accuracy may be attained by completely absorbing the vapour of the water, and collecting the carbon disulphide in alcoholic potash (Delachanal a. Mermet, *Compt. rend.* lxxi. 92).

Another method is founded on the decomposition of alkaline thiocarbonates by arsenious acid. When this acid is added to potassium or sodium thiocarbonate in aqueous solution and the mixture heated, carbon disulphide is volatilised. If this be condensed and conducted into a graduated receiver, the weight of carbon sulphide in the thiocarbonate used may be obtained by multiplying the volume found by its density (David a. Rommier, *ibid.* 86).

A third method, depending on the instability of zinc thiocarbonate, has been proposed by Finot a. Bertrand (*Ann. Chim. Phys.* [5], ix. 142). Ten grams of the alkaline thiocarbonate, together with 25–30 c.c. of water and 10 c.c. of a strong solution of zinc sulphate, are introduced into a flask of about 100 c.c. capacity, fitted up like a carbonic acid apparatus. On mixing the contents of the flask, a yellow precipitate of zinc thiocarbonate is produced, which decomposes slowly in the cold, but very rapidly at a temperature of 50° or 60°, according to the equation $\text{ZnS.CS}^2 = \text{ZnS} + \text{CS}^2$; consequently the loss in weight corresponds with the amount of carbon disulphide contained in 10 grams of the alkaline thiocarbonate.

The thiocarbonates of copper and mercury undergo a similar decomposition.

Carbon disulphide in the free state, as it exists in coal-gas, for example, may be estimated by converting it into potassium xanthate, this salt being then titrated with a normal solution of cupric sulphate at one-fiftieth, containing, therefore, 0.0012672 grm. of copper in a cubic centimeter, which is equivalent to 0.006404 grm. potassium xanthate, and to 0.00304 CS^2 . The normal liquid may also be employed at one-twentieth; 1 c.c. = 0.003168 grm. Cu. To obtain this liquid, 3.168 grms. of cupric sulphate are dissolved in water, the solution is treated with Rochelle salt and sodium carbonate, till the precipitate is redissolved and then diluted to 1 litre. The presence of ammonia and caustic alkalis must be avoided. As potassium xanthate contains an excess of caustic alkali, this excess must be neutralised with cream of tartar, or better with sodium bicarbonate (Grete, *Chem. Centr.* ix. 921; *Chem. News*, lxxvi. 156).

CARBONATES. The carbonates of the alkali-metals may be prepared from the corresponding sulphates by dissolving the sulphates in water containing carbonic acid; adding to the solution a quantity of barium carbonate equal in weight to about 1½ times the sulphate, and rubbed up with water to a thick pulp; agitating the mixture briskly for some time; and finally heating it to the boiling point: the filtrate will then contain nothing but alkaline carbonate (J. Lawrence Smith, *American Chemist*, 1873, iii. 241).

Pure sodium carbonate may be prepared by dissolving 63 grams of commercial oxalic acid in 200 c.c. of warm water, and adding the solution to 200 c.c. of a cold solution of 143 grams of ordinary 'soda crystals.' The sodium oxalate soon crystallises out and is converted into the carbonate by ignition.

To prepare potassium carbonate containing no impurity but a trace of nitrate, 1 pt. of pure nitre and 2 pts. of oxalic acid are mixed in a crucible, and a little water is added. Evaporation is then carried nearly to dryness, water is again added, and the evaporation repeated. The crucible is then heated to redness (J. L. Smith, *Chem. News*, xxx. 234).

The formation of sodium bicarbonate from sodium chloride and ammonium carbonate may be demonstrated by introducing a lump of the latter salt into a cold saturated solution of pure sodium chloride. As the ammonium salt dissolves, the bottom of the vessel becomes covered with a fine white powder, which disappears completely on warming or dilution. The same reaction takes place on mixing the concentrated solutions of sodium chloride and ammonium bicarbonate (A. Vogel, *N. Rép. Pharm.* xxiii. 3).

Solubility and Dissociation of the Acid Carbonates of Potassium, Sodium, and Ammonium.—The loss of carbonic acid when solutions of these salts are exposed to the air has long been noticed. A portion of the salt appears to be decomposed in the solution, and as the carbonic acid passes off, fresh quantities of the salt are successively decomposed, until the whole is transformed into the neutral carbonate. In a closed vessel the carbonic acid first set free tends by its presence to hinder the further evolution of the gas, and the decomposition is arrested with a degree of completeness dependent on the pressure. On the other hand if the layer of gas above the surface of the liquid be constantly removed, either by keeping the vessel in a vacuum, or by passing a stream of air through the solution, the salt will be more rapidly converted into neutral carbonate. Hence crystals of the acid carbonates of potassium and sodium should be dried over sulphuric acid in an atmosphere of carbonic acid gas; otherwise they become covered with a layer of neutral carbonate (Dibbitts, *J. pr. Chem.* [2], x. 417).

As in the determinations hitherto made of the solubilities of the potassium and sodium acid carbonates, the loss of carbonic acid from the crystals and from the solutions has not been taken into account, Dibbitts has undertaken these determinations afresh with samples of the pure salts, operating in vessels securely corked, in which the decomposition of the salt in solution is arrested by the pressure of the carbonic acid gas. He has also determined the percentage of carbonic acid set free at various temperatures, and the solubility of ammonium acid carbonate, which decomposes with much greater readiness than the other two, the pressure of the carbonic acid extricated from a saturated solution at 30° being so great that determinations of the solubilities at higher temperatures could not be made, while in the case of the other two salts the determinations were carried to 60°. The tensions of the gas liberated from saturated solutions of the three salts at 15°, roughly measured in millimeters of mercury above the atmospheric pressure, were, for the sodium, potassium, and ammonium acid carbonates, 130, 461, and 720 respectively. The ammonium salt was prepared by placing the crystals, after pressure in bibulous paper, in an exsiccator filled with air, over sulphuric acid and caustic soda. After some days all the water, free ammonia, and carbonic acid were completely absorbed, and the pure salt remained behind.

The following table, calculated from determinations of the solubility of the three acid salts in water, exhibits the solubility of the potassium and sodium salts for every five degrees of temperature from 0° to 60°, and of the ammonium salt from 0° to 30°:—

Solubility in 100 Parts of Water.

Temp.	KHCO ³	NaHCO ³	(NH ⁴)HCO ³
0°	22.45	6.9	11.9
5	25.0	7.45	13.7
10°	27.7	8.15	15.85
15	30.4	8.85	18.3
20	33.2	9.6	21.0

Solubility in 100 parts of Water—continued.

Temp.	KHCO ³ .	NaHCO ³ .	(NH ⁴)HCO ³ .
25	36.1	10.35	23.9
30	39.0	11.1	27.0
35	42.05	11.9	
40	45.25	12.7	
45	48.6	13.55	
50	52.15	14.45	
55	55.9	15.4	
60	60.0	16.4	

On the Absorption of Acid Carbonates from Natural Waters by Plants, see Barthélemy (*Compt. rend.* xxxii, 548; *Chem. Soc. Jour.* 1876, ii, 113).

Action of Silica and analogous Oxides on Sodium Carbonate.—When silicic acid and sodium carbonate are heated together in a platinum crucible, the loss of carbonic acid is found to tend to a certain limit, different for different temperatures. The rate at which the loss increases with the time may be expressed by the equation—

$$y = \frac{ax}{b + x}$$

where y = loss of carbonic acid, x = time.

The variation of the result with the temperature may be explained on the assumption that at the commencement of the reaction an acid silicate is formed, which decomposes again into neutral silicate and silicic acid, the latter of which acts upon more sodium carbonate, until a state of equilibrium is attained between the neutral and acid silicates and the silicic acid. This equilibrium is of course dependent upon the temperature. A similar explanation applies probably to the action of the bibasic compounds, titan acid and zirconia, upon sodium carbonate. Alumina and ferric oxide, on the other hand, and boric acid behave as monobasic acids; when melted with sodium carbonate they form, immediately or in a few minutes, the compounds $Al^2O^3 \cdot Na^2O$, $Fe^2O^3 \cdot Na^2O$, and $B^2O^3 \cdot 3Na^2O$, and the result is not modified by elevation of temperature (Mallard, *Compt. rend.* lxxv, 472).

On the Action of Aluminium on Sodium Carbonate at High Temperatures, see p. 65 of this volume.

On the Analysis of Carbonates by means of the Carbometer, see Pruett a. Jones (*Chem. Soc. Jour.* 1877, ii, 38).

Action of Alkaline Carbonates on Earthy Oxalates, and of Alkaline Oxalates on Earthy Carbonates.—A solution of ammonium oxalate brought in contact with chalk or powdered marble, is almost instantly attacked, even in the cold; on applying heat, an odour of ammonia at once becomes perceptible, and on boiling it becomes strong. To measure the extent of this reaction, and compare it with the converse action of soluble carbonates on earthy oxalates, the following experiments have been made by Watson Smith (*Chem. Soc. Jour.* 1877, ii, 245).

Sodium oxalate in solution on Calcium carbonate: if the reaction were complete, 5.3 grms. of sodium carbonate would have been formed; in the cold 1.05 grm. were obtained, = 19.83 per cent.; boiling for three hours produced 1.2135 grm., or 22.90 per cent. *Sodium carbonate solution on Calcium oxalate*: in the cold, 16.07 per cent.; boiled for thirty minutes, 52.34 per cent. *Sodium oxalate in excess on powdered marble*: in the cold, 20.07 per cent.; boiling, 26.00 per cent. *Sodium carbonate in excess on Calcium oxalate*: cold, 13.09 per cent.; boiling, 78.35 per cent. By treating the same portion of calcium carbonate with successive quantities of sodium oxalate 45.87 per cent. of sodium carbonate were obtained, the action gradually ceasing. By treating the same quantity of calcium oxalate with successive portions of sodium carbonate 93.83 per cent. was decomposed. *Sodium oxalate on Strontium carbonate*: cold, 7.63 per cent.; hot, 7.63 per cent. *Sodium carbonate on Strontium oxalate*: cold, 67.24 per cent.; hot, 79.06 per cent. *Sodium oxalate on Barium carbonate*: cold, 4.84 per cent.; hot, 4.97 per cent. *Sodium carbonate on Barium oxalate*: cold, 73.20 per cent.; hot, 87.96 per cent. *Ammonium oxalate on Calcium carbonate*: cold, 12.27 per cent.; with excess of oxalate, 13.53 per cent.; with excess of carbonate, 10.94 per cent. *Sodium oxalate on Lead carbonate*: cold, 6.35 per cent.; hot, 13.08 per cent. *Sodium carbonate on Lead oxalate*: cold, 81.54 per cent.; boiling, 90.61 per cent.

Decomposition of Insoluble Carbonates by Hydrogen Sulphide.—When barium carbonate suspended in water at 10° is treated with a slow current of hydrogen sulphide, it is gradually converted into barium sulphide, the conversion being partial or complete according to the proportion of water present. Thus, of 100 parts of the

carbonate suspended in 10 times its weight of water, 15.3 parts were converted into sulphide in five hours; of the same quantity of carbonate suspended in 50 times its weight of water, 51.2 parts were converted into sulphide in six hours; whilst carbonate suspended in 100 times its weight of water was completely converted into sulphide in thirty hours. The solution of barium sulphide formed was colourless at first, but turned yellow in the air.

Magnesium, zinc, and lithium carbonates behaved in the same manner as barium carbonate (Naudin a. De Montholon, *Compt. rend.* lxxxiii. 58).

Ammonio-silver Carbonate, $\text{Ag}^2\text{CO}^1.4\text{NH}^3$. This salt is obtained as a grey precipitate on adding absolute alcohol to a solution of silver carbonate in aqueous ammonia of sp. gr. 0.930. It becomes darker when dried, is blackened and ultimately dissolved by ammonia, and deposited in regular crystals when the ammoniacal solution is dried over calcium chloride. The dry salt begins to give off ammonia at 80° , but the evolution ceases at 100° , and at 160° – 170° , the residue becomes a uniform black mass which decomposes completely at 305° , leaving metallic silver (S. Kern, *Chem. News*, xxxi. 231).

Calcium Carbonate. The action of sulphur on this salt has been studied by Pollacci (*Gazz. chim. ital.* 1874, pp. 177, 425, 469). The formation of calcium sulphate in soils containing the carbonate and sulphur was explained by Dumas, on the supposition that the sulphur in contact with the organic matter of the soil produces hydrogen sulphide, which is subsequently oxidised to sulphuric acid. Pollacci, however, finds that sulphur can convert sulphates into carbonates without the intervention of organic matter, and without previous formation of hydrogen sulphide. Perfectly pure precipitated calcium carbonate and flowers of sulphur freed from sulphuric acid were made into a thin paste with water, and placed in sunshine, the temperature being about 40° , for four hours. The dried mass was then found to be rich in sulphate. Another experiment showed that sunlight is not necessary to the reaction. The presence of such organic matter as humus, or of horse-dung, hastens it. Pollacci considers that the greater part of the calcium sulphates of soil has been formed by this reaction, and that when the formation of hydrogen sulphide has been one stage in the production of the sulphate (e.g., from organic matter which has decayed, or from volcanic sources), the acid is first decomposed into water and free sulphur. He points out that sulphate is an invariable constituent of the soil in the districts whence sulphur is obtained, and that the rock which is nearly always closely associated with the sulphur (*briscate* or *madre dello zolfo*) is a calcium sulphate. Moreover, analyses by different chemists of an Italian, a French, and a German soil, each containing free sulphur, agree in this, that the soils contained abundance of sulphate, but no carbonate. All the alkaline-earth carbonates behave like calcium carbonates with sulphur and water, though with different degrees of intensity. Barium, strontium, and magnesium are also found associated with sulphur as sulphates, but not as carbonates.

According to Brugnatelli a. Pelloggio (*Gazz.* 1874, 586) the oxidation of the sulphur under the circumstances above described, takes place at the expense of the oxygen of the water and not, as supposed by Pollacci, through the agency of atmospheric oxygen, and the formation of sulphuric acid is preceded by that of pentathionic and tetrathionic acids. See also Bellucci (*Gazz.* 1874, p. 179).

On the action of Calcium Carbonate on Calcium Phosphate and Superphosphates, see Jaffre (*Monit. Scient.* [3], iv. 1065).

A gelatinous hydrate of calcium carbonate is formed by the action of carbonic acid on lime and water (Bondonneau, *Bull. Soc. Chim.* [2], xxiii. 100).

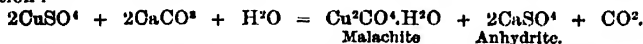
Copper Carbonates (F. Weibel, *Jahrbuch f. Mineralogie*, 1873, 246). Nearly all the published analyses of azurite indicate a difference between the actual composition of the mineral and that which it should have in accordance with the formula— $\text{Cu}^2\text{CO}^1 + \text{H}^2\text{O}$, or $3\text{CuO}.2\text{CO}^2 + \text{H}^2\text{O}$, viz., 69.2 per cent. CuO, 25.6 CO^2 , and 5.2 H^2O , the carbonic anhydride found being less than the calculated amount by 0.1 to 1.56 per cent., and the water in excess of the calculated quantity by 0.24 to 1.28 per cent. A specimen of massive-crystalline azurite from Siberia, freed as completely as possible from gangue and admixed malachite, carefully dried over sulphuric acid at 100° , gave by analysis, after deduction of 4.06 per cent. insoluble admixtures (ferric oxide, silica, &c.), 69.66 per cent. CuO, 24.26 CO^2 , and 6.08 water. This result, like that of all previous analyses, indicates a composition intermediate between that of azurite and that of malachite, $2\text{CuO}.\text{CO}^2 + \text{H}^2\text{O}$ (71.9 per cent. CuO, 19.9 CO^2 , 8.2 H^2O), and leads to the supposition that azurite may be formed from malachite by abstraction of water and addition of carbonic anhydride, a supposition further suggested by the fact that azurite and malachite almost invariably occur together.

That azurite may actually be formed from malachite in this manner is shown by

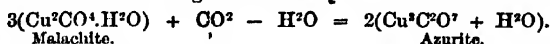
the following experiment. Small pieces of marble were introduced, together with a moderately strong solution of cupric sulphate, into a tube of Bohemian glass, which was then sealed and heated to 150° – 190° for about 24 hours. On removing the tube from the air-bath, the liquid was found to be completely decolorised, and the lumps of marble were covered with a crust of malachite of a fine green colour. This, indeed, is a well-known result. But further, on setting the tube aside, still closed, and at the temperature of the air, small crystals of gypsum began to separate after about a week, their quantity continually increasing for several weeks more, while at the same time the liquid almost entirely disappeared, and the green crust of malachite on the marble became dotted with small dark blue nodules, which gradually increased till they formed in some parts a compact coating. On opening the tube after about three-quarters of a year, no tension was found inside. The dark blue substance was easily recognised as a copper carbonate, but no quantitative analysis was made of it, on account of the difficulty of obtaining it in sufficient quantity free from the malachite to which it adhered; but the dark blue colour and the crystalline character* of the nodules* afford sufficient proof that they consist of azurite.

The mode of action in this experiment is easily understood. The mutual action of the calcium carbonate and copper sulphate at a high temperature produces copper carbonate (malachite), calcium sulphate, and carbonic anhydride. The calcium sulphate is at first held in solution, not as gypsum but as anhydrite; otherwise it would crystallise out as gypsum, either during the heating of the tube, or at all events during cooling, especially as its quantity is somewhat considerable; since, however, the actual separation of the gypsum is very gradual, we must suppose that it is slowly formed after cooling by combination of the anhydrite with water.

The first stage of the process above described may accordingly be represented by the equation:



As soon as the tube cools, the anhydrite begins to be transformed into gypsum by assumption of water, which it ultimately takes from the malachite, this latter compound at the same time absorbing carbonic anhydride which is present in a state of high tension, the final result being the conversion of the malachite into azurite—



This mode of formation of azurite may be thus expressed: *Azurite is formed from malachite at ordinary temperatures by addition of carbonic anhydride and abstraction of water, in presence of carbonic anhydride of high tension and a dehydrating agent.*

The assumption that native azurite is formed in this manner appears at first sight somewhat in discordance with the fact that pseudomorphs of malachite after azurite are of frequent occurrence, whereas pseudomorphs of azurite after malachite are never found. But the formation of malachite from azurite by assumption of water and loss of carbonic acid—which undoubtedly takes place—by no means precludes the possible formation of azurite from malachite under different external conditions; and on the other hand the non-occurrence of pseudomorphs of azurite after malachite is sufficiently accounted for by the rarity of crystals of the latter mineral.

Lead Carbonate. This salt has been formed in the crystallised state on the bases of some bronze objects, discovered at Pompeii, which had been loaded with lead. In some of these the carbonate appears simply as an amorphous mass; in others the amorphous mass is accompanied by carbonic acid in a translucent and compact state, with incipient traces of crystallisation; and in one case the carbonate occurs in brilliant and well defined crystals, which must have been formed within a known interval of time (S. de Luca, *Compt. rend.* lxxiv. 1457).

Lead carbonate is soluble in *neutral ammonium butyrate*, a solution of 100 grams of that salt at 10° , taking up 1.038 grams of lead carbonate in six minutes, and 1.536 grams in four days. The solution is limpid and colourless, and might afford a means of obtaining lead carbonate in crystals (Bartrand, *J. Pharm. Chim.* [4], xxxiii. 346).

Magnesium Carbonate. According to E. Fleischer (*J. pr. Chem.* [2], vi. 273), this salt is partially decomposed by calcium sulphate solution, especially in presence

* A similar result was obtained some years ago by Debray (*Jahresber. f. Chemie*, 1859, 214), who enclosed lumps of chalk, together with solid cupric nitrate and water, in a sealed tube, and found that, on leaving the tube to itself at the ordinary temperature, the chalk became covered with a green crust of basic cupric nitrate, on which blue crystalline nodules of azurite gradually formed. The carbonic anhydride in the tube evolved by the decomposition of the chalk exhibited a pressure of three to four atmospheres.

of common salt, into calcium carbonate and magnesium sulphate. When equivalent quantities of gypsum (5.0 grams of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$) and *magnesia alba* (3.8 grams) were digested for an hour with common salt (1 : 6, 100 c.c.) in a water-bath at 80° , the water being renewed as it evaporated, about 30 per cent. of the gypsum was converted into calcium carbonate, and 15 per cent. dissolved in the solution of common salt. When the same quantities of magnesium carbonate and gypsum were treated with a 1 : 12 solution of common salt, 28 per cent. gypsum was decomposed and only 10 per cent. dissolved. If to the solution of common salt, magnesium sulphate (19.230 grams) be added (whereby sodium sulphate and magnesium chloride are formed), the decomposition of the gypsum, though not completely arrested, is greatly retarded. An increase of the proportion of common salt to gypsum does not produce more favourable results. When a solution of common salt is left to act on magnesium carbonate and gypsum at ordinary temperatures, only about 8.4 per cent. of the gypsum is decomposed.

Magnesium carbonate dissolves in cold solutions of *alkaline borates*, is precipitated therefrom on heating, and disappears again as the solution cools (Wittstein, *Arch. Pharm.* [3], vi. 40).

CARBONYL-DISULPHETHYL, PROPYL, &c. See THIOCARBONIC ETHERS.

CARBONYL-DISULPHODI-

CARBONYLS. This name is proposed by Berthelot (*Compt. rend.* lxxix. 1093), for certain compounds which he regards as aldehydes of a new class, comprising at present three members, namely, ordinary camphor, $\text{C}^{10}\text{H}^{16}\text{O}$, allylene oxide or dimethylene-carbonyl, $\text{C}^2\text{H}^2\text{O}$, and diphenylene-carbonyl, $\text{C}^{12}\text{H}^8\text{O}$ (diphenylene-ketone). Suberone, $\text{C}^{12}\text{H}^{12}\text{O}$, probably possesses a similar constitution.

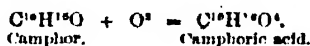
These bodies are characterised by the following general properties :—

1. They unite directly with hydrogen, producing alcohols, from which the carbonyls may be regenerated by oxidation.

2. They are formed by substituting O for H^2 in certain unsaturated hydrocarbons.

3. By union with the elements of water they furnish monobasic acids, the typical reaction being the production of formic acid from carbonic oxide.

4. The carbonyls can be converted into bibasic acids by fixation of three atoms of oxygen, e.g. :—



These bodies are thus distinguished both from primary aldehydes, the oxidation of which results in the production of a single monobasic acid, and from secondary aldehydes, or ketones, which, when oxidised, generally yield two distinct acids.

CARBOTHIALDINE, $\text{C}^8\text{H}^{10}\text{N}^2\text{S}^2$. On the formation and constitution of this compound, see p. 387.



This acid, which Griess obtained by the action of heat on uramidobenzoic acid (*2nd Suppl.* 166), is also produced by adding potash or soda in excess to a mixture of thiocarbamidobenzoic acid (p. 269) and mercuric oxide, suspended in boiling water. The whole of the sulphur is thereby removed, and the filtrate, largely diluted with water, and supersaturated with hydrochloric acid at the boiling heat, yields an amorphous or micro-acicular precipitate of carboxamidobenzoic acid.

CARBOXYPHENYL-TOLYL-TRICHLORETHANE, $\text{C}^{16}\text{H}^{18}\text{Cl}^3\text{O}^2$:—
 $\text{C}^6\text{HCl}^3 < \text{C}^6\text{H}^4 \cdot \text{CH}^2 < \text{C}^6\text{H}^4 \cdot \text{CO} \cdot \text{H}$. A monobasic acid, produced by oxidising dimethyl-phenyl-trichlorethane, $\text{O}^2\text{HCl}^3(\text{C}^6\text{H}^4 \cdot \text{CH}^3)^2$, with chromic acid. It crystallises from alcohol in small plates melting at 173° – 174° . Its alkali-salts crystallise well; the barium, calcium, and magnesium salts are flocculent precipitates (O. Fischer, *Deutsch. Chem. Ges. Ber.* vii. 1191).

CARMINE ACID. The red colour of this acid is destroyed by iodine in presence of alkalis. The reaction is suggested as applicable to the testing of carmine and to the estimation of iodine (A. Frebault, *J. Pharm. Chim.* [4], xxiii. 338).

The root of this plant contains a small quantity of an alkaloid not yet examined, together with an acrid resin, a red colouring matter, tannin, and a volatile oil (E. L. Cleaver, *Pharm. J. Trans.* [3], v. 966).

CARNINE, ($C^8H^8N^2O^3$) (2nd Suppl. 269). This base has been found, together with xanthine, guanine, hypoxanthine, sarcine, and other bodies, in the extract obtained by boiling yeast with water¹ (Schutzenberger, *Compt. rend.* lxxviii. 493).

CAROB. The carob bean, or St. John's bread, the fruit of *Ceratonia siliqua*, contains isobutyric acid, but the portion left behind on distillation with water yields normal butyric acid when fermented with chalk and cheese (2nd Suppl. 227).

CARPENE, C^8H^{14} . A hydrocarbon, obtained, together with paracresol, by distilling the calcium salt of podocarpic acid (*q. v.*) It resembles the terpenes; smells like turpentine and storax; boils at 155° – 157° ; becomes resinised on exposure to the air, yielding an oxidised product, $C^{14}H^{26}O^2$; and when treated with bromine, yields bromocarpene, $C^8H^{15}Br$ [$? C^8H^{13}Br$] (Oudemans, *Deut. Chem. Ges. Ber.* vi. 1125).

CARVACROL, $C^{10}H^{16}O$. See PHENOL, HOMOLOGUES of (2nd Suppl. 935).

CARYOPHYLLIC ACID, $C^{20}H^{32}O^4$. An acid obtained by treating caryophyllin with fuming nitric acid; whereupon it dissolves with evolution of heat, the mixture after a short time solidifying to a pulp of microscopic white needles. When purified, first by solution in ammonia and reprecipitation by an acid, and then by repeated precipitation of its alcoholic solution by water, the caryophyllic acid is obtained in the amorphous state. It dissolves in water with difficulty, readily in alcohol, ether, and glacial acetic acid, from all of which it separates in the amorphous state. It may, however, be crystallised from fuming nitric acid.

Sodium Caryophyllate, $C^{20}H^{30}Na^2O^4$.—Caryophyllic acid decomposes sodium carbonate, and on evaporating the solution to dryness and extracting with alcohol, an amorphous sodium-compound of the new acid is obtained.

Silver Caryophyllate, $C^{20}H^{30}Ag^2O^4$, is obtained as a yellow amorphous powder on precipitating a solution of the sodium salt with silver nitrate.

Barium Caryophyllate, $C^{20}H^{30}BaO^4 + 1\frac{1}{2}H^2O$, is a yellowish precipitate insoluble in alcohol, sparingly soluble in water (Mylius, *Deut. Chem. Ges. Ber.* vi. 1053).

CARYOPHYLLIN, $C^{24}H^{40}O^2$. The formula $C^{10}H^{16}O$, usually assigned to this substance (i. 809) should be doubled, inasmuch as the temperature at which it sublimes (285°) is much higher than that at which common camphor distils (204°). The doubled formula likewise agrees better with that of caryophyllic acid. Contrary to ordinary statement, caryophyllin is completely insoluble in alkaline liquids (Mylius).

CASCARILLIN. This substance, the bitter principle of cascarilla bark (i. 809), is said by Tuson (*Chem. Soc. J.* xvii. 195), to be very similar to ricinine, the alkaloid of castor-oil seeds. According to C. and E. Mylius, however (*Deut. Chem. Ges. Ber.* vi. 1051), this alleged resemblance does not exist, ricinine being a well characterised alkaloid, whereas cascarillin is a neutral body having the empirical composition $C^8H^8O^2$. Cascarillin is acted upon by bromine and by nitric acid, but the products have not been obtained in definite form. It is not split up by boiling with dilute acids, and therefore is not a glucoside.

CASSIA. The chemical constituents of the bark of *Cassia lignea* have been examined by P. Trojanowsky (*Russ. Zeitschr. Pharm.* 1874, 418); 100 pts. of the dried powder of two samples were found to contain:

Essential oil	4.45	1.17
Resin soluble in ether	1.30	0.76
Resin insoluble in ether	16.49	5.85
Tannic acid	2.03	3.12
Starch	5.70	—
Mucus	5.12	2.78
Ash	3.97	2.06

CASSITERITE, SnO^2 . On pseudomorphic crystals of cassiterite after orthoclase, from Huel Coates in the parish of St. Agnes, Cornwall, see J. A. Phillips (*Chem. Soc. J.* 1875, 684).

CASTOR OIL. The products obtained by saponifying this oil, and distilling the resulting alkaline ricinoleate alone, or with excess of alkali, have been carefully examined by Neison (*Chem. Soc. J.* [2], xii. 507, 837), whose results are in accordance with those previously obtained by Bouis and by Städeler (*v.* 110), viz., that sodium ricinoleate, when distilled alone, yields a distillate of heptylic aldehyde (œnanthol), but that when the same salt is distilled with excess of alkali, it yields a distillate of secondary octyl alcohol or methyl-hexyl carbinol and methyl-hexyl ketone, and a residue of sodium sebate.

Testing.—Pure castor oil when mixed with 5 vol. alcohol of 90 per cent. gives a clear solution, whereas if any fatty oil be present even 10–20 times the volume of spirit will fail to do so.

To estimate the amount of affixed fat, shake at a temperature of 30° a portion of the oil with twice its volume of 90 per cent. alcohol. Upon cooling, and when at rest, it will separate into three layers, the lowest of which is generally the foreign oil. This gives a tolerably accurate determination of the quantity of admixed oil (Hager, *Chem. Centr.* 1876, 389).

CATALYSIS. The following mechanical explanation of catalytic phenomena is proposed by G. Hüfner (*J. pr. Chem.* [2], x. 386). Chemical molecules are supposed to be rigid compounds, or systems which can be disintegrated, but can neither revolve, nor be moved from their places as a whole.

If two molecules, each consisting of two atoms, come so near each other that they enter into each other's spheres of mutual chemical influence, each atom exerts an attractive force on each of the other three. If the attraction between the atoms of the first molecule is greater than the resultant of the attractions which tend to separate the atoms, no decomposition takes place. In other cases the molecule is split up, and if then the attractive force between the atoms of the second molecule is less than the corresponding resultant of the forces acting in opposition to it, it is also broken up; in the other cases, on the contrary, where the attractive force between the atoms of the second molecule is greater than this resultant, the second molecule remains intact, and only the first one is decomposed. These suppositions may be extended to three or more molecules, and lead to the conclusion that relative intensities may be conceived to exist between attractive forces, which may bring about the decomposition of two molecules out of three, which influence each other, and not of the third, or of one of two, and not of the other. After decomposition, the single atoms may arrange themselves in new chemical combination.

CATECHIN. The results of analyses of this substance from different sources and by different chemists are by no means accordant. The following formulæ have been assigned to it (*1st Suppl.* 416):

Hlasiwetz a. Mallin	Zwenger	Neubauer	Kraut a. van Delden	Loewe	Schützenberger a. Rack
$C^{12}H^{10}O^8$	$C^{12}H^{10}O^8$	$C^{12}H^{10}O^7$	$C^{12}H^{12}O^8$	$C^{12}H^{14}O^7$	$C^{12}H^{12}O^8$

According to Gautier (*Compt. rend.* lxxxv. 342), the catechins obtained from yellow and brown catechu (the produce of *Acacia Catechu*) contain, when dried at 120°, from 62.97 to 63.17 per cent. carbon, and 4.15 to 4.62 hydrogen, and may be represented by the formula $C^{12}H^{10}O^8$, which requires 63.31 C. and 4.62 H.; but the catechin from yellow catechu contains, after drying in a vacuum, 3 mols. water of crystallisation, which it gives off at 120°, and then melts at 188°–191°, whereas that from brown catechu gives off 4 mol. H^2O in a vacuum, and then melts at 140°; hence Gautier regards them as different substances. Catechin from mahogany (*bois d'acajou*) also dried at 100°, gave 63.29 C. and 4.31 H.; at 136°, 63.10 C. and 4.39 H., whence Gautier deduces the formula $C^{12}H^{10}O^8 - 2C^{12}H^{10}O^8 - H^2$. Latour a. Caseneuve (*Bull. Soc. Chim.* [2], xxiv. 119) found this tannin, dried at 100°, to contain 59.43 per cent. C. and 6.00 H., whence they deduced the formula $C^{12}H^{10}O^8$ (59.44 C. and 4.95 H.), differing from Zwenger's formula by $+H^2O$. Makogany catechin melts, according to Gautier, at 166°.

From recent experiments by Etti, however (*Liebigs Annalen*, clxxxvi. 327), it appears highly probable that the discrepancies in the results above mentioned are due to the methods of drying adopted by the several experimenters. Catechin, in fact, when heated for some time to 100°, and even when kept over sulphuric acid in a vacuum at ordinary temperatures, gives off, not only its water of crystallisation, but an additional quantity, giving rise to an anhydride, $C^{12}H^{10}O^8 - 2C^{12}H^{10}O^8 - H^2O$, and when heated to about 160°, it yields a second anhydride, $2C^{12}H^{10}O^8 - 2H^2O$; hence, as all the analyses above quoted were made upon catechins dried at 100° or upwards, it is probable that they represent the composition, not of definite substances, but of mixtures of catechin with one or more of these anhydrides.

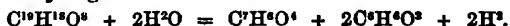
To prepare pure catechin, Etti proceeds as follows: Catechu is dissolved in eight times its weight of boiling water, and the liquid, after being strained through a cloth, is left for some days till the insoluble catechin has subsided. The crude catechin is collected in a linen cloth, and submitted to the action of a screw-press, then dissolved in a sufficient quantity of dilute alcohol, and the filtered solution is shaken up with ether as long as any catechin is thereby dissolved; and after the ether has been removed by distillation, the residue is taken up with distilled water, and the solution is left for a few days, when the catechin crystallises out in an almost colourless state.

After pressure in a cloth it is again dissolved in boiling water, when a yellowish-white body remains behind, which appears to be quercetin. The deep red liquid remaining after the catechin has been dissolved out by ether, contains catechin-red.

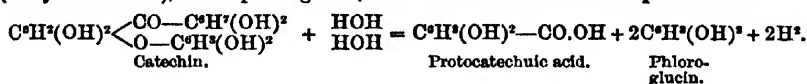
The catechin prepared as above was freed from its water of crystallisation by leaving it for a few days over sulphuric acid (not in a vacuum), or by drying at 80–90°. It then gave by analysis 60.66 to 60.97 per cent. carbon and 4.83 to 5.10 hydrogen, agreeing very nearly with the formula $C^{12}H^{10}O^4$, previously given by Hlasewitz a. Malin, which requires 60.95 C. 4.81 H. and 34.24 O.

Catechin thus obtained precipitates albumin, but not gelatin. Its aqueous solution is not altered by boiling with zinc and sulphuric acid. It does not immediately expel CO^2 from barium carbonate at boiling heat, but a small quantity of that gas is evolved on prolonged boiling, because the catechin is thereby converted into the mono-anhydride, which has the power of decomposing carbonates.

Catechin fused with potassium hydrate is resolved into protocathechuic acid, phloroglucin and 2 mols. hydrogen:



This reaction, together with the composition of the anhydrides described below, indicate that it contains the residues of a tetrahydrogenised protocathechuic acid, $C^7H^4O^4$ (not yet obtained), and diphloroglucin, united in the manner of the phthaleins:



Anhydrides of Catechin. These bodies are formed by the combination of two molecules of catechin, with elimination of 1, 2, 3, and 4 mols. of water.

The Mono-anhydride, $C^{12}H^{10}O^{13} = 2C^{12}H^{10}O^4 - H^2O$, also called *Catechin-red* and *Catechutannic acid*, may be prepared by drying catechin for several days in a vacuum over sulphuric acid, and afterwards heating it in an air-bath to 127°; it then loses about 2.40 per cent. of its weight, which is that required by the formula above given, and suffers no farther loss at 160°. The same compound is quickly formed by boiling catechin with aqueous sodium carbonate. It is also produced, as already observed, in the preparation of catechin from catechu, remains dissolved in the deep-red alcoholic liquid after the catechin has been removed by agitation with ether, and is deposited, on evaporating off the alcohol and ether, and leaving the liquid to cool, in the form of a red precipitate which may be collected on a linen filter, washed with water, and pressed. It still, however, retains inorganic matters (iron oxide, lime, and magnesia), from which it may be freed by dissolving it in a small quantity of very dilute alcohol, adding pure hydrochloric acid previously diluted with 2 pts. water, leaving the liquid at ordinary temperatures for some hours at the temperature of the air, with frequent agitation, then diluting it with water, as long as a red precipitate is produced. This precipitate is collected on a cloth, strongly pressed, and dissolved in alcohol. The filtered alcoholic solution, on evaporation, leaves the catechin-red, which, when triturated, forms a shining black-red powder.

This anhydride, while still moist, is moderately soluble in water, and is precipitated therefrom by dilute acids; it dissolves very easily in alcohol at all degrees of dilution, but is insoluble in ether. When quite freed from moisture it does not dissolve in either of these liquids. When dissolved in water it completely precipitates both albumin and gelatin from their solutions, and must therefore be regarded as a tannin: hence it is appropriately named *Catechutannic acid*. It exhibits also the characters of an acid and decomposes carbonates. With the alkalis it forms salts easily soluble in water; with baryta and lime, insoluble salts.

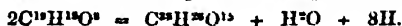
The Dianhydride, $C^{12}H^{10}O^{14} = 2C^{12}H^{10}O^4 - 2H^2O$, may be prepared by heating the monoanhydride up to 162°, or by boiling it for several hours with dilute sulphuric acid. It resembles the monoanhydride in its behaviour to solvents, alkalis, carbonates, albumin, and gelatin. It may be heated to 190° without change, but at 210° it begins to carbonise.

The Trianhydride, $C^{12}H^{10}O^{15} = 2C^{12}H^{10}O^4 - 3H^2O$, is prepared by boiling catechin with dilute sulphuric acid (1 : 24). After a time a reddish-yellow precipitate separates out, which, when washed and perfectly dried, becomes of a dark reddish-brown colour. It is perfectly insoluble in water, alcohol, ether, and caustic potash.

The Tetranhydride, $C^{12}H^{10}O^{16} = 2C^{12}H^{10}O^4 - 4H^2O$, also called *Catechuretins*, was discovered in 1863 by Kraut a. van Delden (1st Suppl. 416), who prepared it by passing hydrogen and hydrochloric acid gas simultaneously

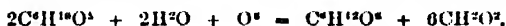
into a boiling alcoholic solution of catechin. Etti prepares it by acting for half a day on catechin with concentrated hydrochloric acid in a sealed tube at 160° to 180° . It consists of a dark reddish-brown powder, which resembles the previous anhydride in solubility. It may be heated to 190° without change. When a small quantity was heated to 190° – 210° and treated with dry hydrochloric acid gas, traces of pyrocatechin were obtained.

Action of Potash on Catechin.—When catechin is boiled with a concentrated solution of caustic potash, a body is obtained which differs from the first anhydride only in the amount of its hydrogen. The decomposition is represented by the equation:



This body behaves towards solvents in the same way as catechin mono-anhydride. Its aqueous solution precipitates albumin and gelatin. When fused with potash it yields only slight traces of phloroglucin and protocathechuic acid. A dianhydride of similar character is obtained by heating this mono-anhydride to 165° – 170° , $C^{12}H^{12}O^{11} - H^2O = C^{12}H^{12}O^{11}$ (Etti).

CELLULOSE. This substance treated with potassium permanganate, or potassium dichromate, and acetic acid, is converted into glucose, dextrin, and formic acid. The production of glucose and formic acid is represented by the equation:



Iron in contact with air and water acts on cellulose, producing glucose, and a gummy substance which is insoluble in alcohol and is converted into glucose by boiling with dilute sulphuric acid. The soluble ferment of foxglove converts cellulose into glucose and dextrin (Kosmann, *Bull. Soc. Chim.* [2], xxvii. 246).

On the Estimation of Cellulose in Plants. See VEGETABLE TISSUE.

On Cellulosic Fermentation. See FERMENTATION.

Cellulose Hydrate, $C^{12}H^{22}O^{11} - 2C^6H^{10}O^5.H^2O$.—This is a brittle structureless substance formed, under certain conditions, by the action of acids on cellulose. Purified cellulose immersed for twelve hours in sulphuric acid of 45° B., does not lose its structure till it is pressed, but it then becomes disintegrated. The product, which is cellulose hydrate, may be washed and dried, but easily crumbles between the fingers. It dissolves in dilute potash, and is easily oxidised. When kept for several days at 50° it turns yellow, and then yields to water a coloured substance which reduces potassio-cupric tartrate or silver nitrate. Cellulose hydrate is also formed when cellulose is heated to 100° with very dilute acids (Girard, *Compt. rend.* lxxxi. 1105).

CEMENT. On the changes which take place in the setting of Portland Cement, see Erdmenger (*Dingl. pol. J.* ccxv. 538; ccxvii. 63; *Chem. Soc. J.* 1876, i. 124).

On Basic Calcium Carbonate in Hydraulic Cements: Schulatschenko (*Dingl. pol. J.* ccv. 335; *Chem. Soc. J.* 1873, 97).

On the Causes which Modify the Setting of Plaster, and on new Cements of Plaster and Lime: Landrin (*Compt. rend.* lxxix. 658; *Chem. Soc. J.* 1875, 106).

On Scott's Selinitic Mortar: F. Schott (*Dingl. pol. J.* ccix. 30; *Chem. Soc. J.* 1874, 96). On Portland Cement from Dolomitic Limestone: Erdmenger (*Dingl. pol. J.* ccix. 386; *Chem. Soc. J.* 1874, 96).

On Cement for Caustic Lye Tanks: *Dingl. pol. J.* ccx. 399; *Chem. Soc. J.* 1874, 106). Cements for Gas-retorts: Capitaine (*Dingl. pol. J.* ccxv. 186; *Chem. Soc. J.* 1875, 130). Cement for Glass and Porcelain: Lieuegang (*Chem. Centr.* 1872, 398; *Chem. Soc. J.* 1873, 97).

According to Goble (*J. Pharm.* [4], xix. 346), Liebreich's protagon (iv. 737) is a mixture of lecithin and cerebrin, a view previously proposed by Strecker (*1st Suppl.* 779). Cerebrin exists largely in brain-matter, from which it is extracted by boiling alcohol. It may be freed from fatty matter by ether, and from lecithin and calcium phosphate by repeated solution in boiling alcohol. It is a solid, inodorous, colourless body. It melts when dry between 165° and 180° , and above the latter temperature turns brown and decomposes, giving off ammoniacal vapours and leaving a deposit of carbon. It is insoluble in water, either cold or boiling, but boiling water causes it to swell into a starch-like mass. From boiling alcohol it separates almost entirely on cooling. Ether has but little action upon it. It combines with acids, and retains traces of them with great stubbornness. It combines also with metallic oxides, but not in definite proportion. Its composition is: C. 66.85, H. 10.82, N. 2.29, O. 20.04.

Bourgoin points out that the centesimal composition of cerebrin agrees with that

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of a compound of ammonia with two equivalents of a dioxyoleic acid, or with a compound of neurine, or some analogous substance, with a fatty acid similar to palmitic acid (*J. Pharm. Chim.* [4], xx. 26).

CERITE. This mineral has mostly been found in amorphous masses. Crystals of cerite having the form of short six-sided prisms are indeed mentioned by Haidinger, but their form was not exactly determined. Recently, however, A. E. Nordenskiöld has discovered, in the mineral collection of the Mining School at Stockholm, distinct crystals of cerite, enclosed, together with small crystals of allanite, in bismuth-glance.

These crystals, which belong to the rhombic system, form grains resembling chondrodite, not larger than peas, and bounded by numerous faces, the most distinct of which are ∞P , $\infty P_{\frac{1}{2}}$, ∞P_{∞} , ∞P_{∞} , \bar{P}_{∞} . Axes $a : b : c = 1 : 0.9988 : 0.8127$. Analysis showed that they have the composition of cerite containing a small quantity of fluorine. They contain a very variable amount of water (3.5 to 9 per cent.), perhaps not originally belonging to them.

Supposing then cerite to be anhydrous, it may be regarded as both stoichiometrically and crystallographically isomorphous with olivine:

Olivine (Mg, Fe) 2 SiO $_3$, rhombic, $a : b : c = 1.0729 : 1 : 1.2528$

Cerite (Ce, La, Di, Fe) 2 SiO $_3$, rhombic, $a : b : c = 1.0015 : 1 : 1.2206$

(Nordenskiöld, *Deut. Chem. Ges. Ber.* vii. 476).

CERITE METALS. Ce, Di, La. Mendeleeff, as already stated (*2nd Suppl.* 273), assigns to these elements the atomic weights, Ce = 138 : Di = 138 : La = 180, according to which cerium and didymium are triads and lanthanum is a tetrad.* The number assigned to cerium is corroborated by Mendeleeff's determination of the specific heat of the metal, viz. .050; for this number multiplied by 138 gives for the atomic heat the number 6.9, which is in accordance with the law of Dulong and Petit. This result is confirmed by the recent experiments of Hillebrand (*Pogg. Ann.* clviii. 71), who finds for the specific heat of cerium the value .04479, which is nearly equal to that obtained by Mendeleeff. For the specific heats of didymium and lanthanum also, Hillebrand finds values which, according to the law of Dulong and Petit, give for the atomic weights of these metals values $1\frac{1}{2}$ times as great as those hitherto assigned to them (e.g. for lanthanum, 139 instead of 93.6), and accordingly show that these two metals, hitherto supposed to be dyads, should also be regarded as triads. Hillebrand's numerical results for the three metals are as follows:

	Ce	La	Di
Specific Heat	0.04479	.04485	.04563
Atomic Weight	138	139	144.78
Atomic Heat	6.18	6.23	6.60

Hillebrand, therefore, agrees with Mendeleeff with respect to the quantivalence of cerium and didymium (both triads), but differs from him with respect to lanthanum, which, according to Mendeleeff, is a tetrad. Mendeleeff's conclusion with regard to this metal is not however based on a determination of the specific heat, or indeed on any actual experimental evidence, but merely on what he supposes ought to be the place of lanthanum in the series of elements, according to the periodic law of the atomic weights (*2nd Suppl.* p. 463).

Rammelsberg, as already observed (*2nd Suppl.* 273), raised objections to the changes proposed by Mendeleeff in the atomic weights of the cerite metals, founded partly on the composition of the ceroso-ceric salts, partly on the isomorphous relations of the three metals. Mendeleeff, on the other hand (*Liebig's Annalen*, clxviii. 45; *Jahresbericht*, 1873, 262), defends the proposed changes, on the ground of the greater simplicity of the formulæ based on the new atomic weights, especially in the case of the cerium salts; and with regard to the nonconformity of the formulæ of certain compounds of these metals with those of other compounds which crystallise in similar forms, he observes that, since cases of isomorphism are known to exist between compounds of well-established composition containing unequal numbers of atoms, e.g. ZnO and Al $_2$ O $_3$, CaCO $_3$ and K $_2$ IrF $_6$, FeNb $_2$ O $_6$ and FeWO $_4$, NH $_4$ X and KX—the isomorphism of Ce $_2$ O $_3$ and Fe $_2$ O $_3$, and of Di 2 (SO $_4$) $_3$ + 8H $_2$ O with Cd 2 (SO $_4$) $_3$ + 8H $_2$ O, cannot be regarded as an objection against the adoption of the new atomic weights. The isomorphism of the lanthanum salts with the corresponding didymium salts and

* In his Tables of the Elements arranged according to the Periodic Law, Mendeleeff places cerium as well as lanthanum among the tetrads (*2nd Suppl.* 463, 464).

cerous salts is quite in accordance with the views of their constitution now entertained, Lanthanum having been shown to be a triad, not a tetrad as formerly supposed by Mendelejeff. But it is not necessary to pursue the discussion further, since Rammelsberg himself, in a recent paper (*Deut. Chem. Ges. Ber.* ix, 1680), has withdrawn his objections to the new atomic weights, regarding the question as completely settled by Hillebrand's determinations of the specific heats, and further considering that the new atomic weights have the advantage of affording on the whole simpler formulae for the compounds of the three metals, especially of the ceric salts.

The gadolinite metals, yttrium and erbium, are, in like manner, regarded by Rammelsberg and Mendelejeff as triads. Cleve also (*Bull. Soc. Chim.* [2], xxi, 196, 246) regards the metals of both these groups as triads. Delafontaine, on the other hand (*N. Arch. ph. nat.* li, 45), maintains the older view, partly from considerations of isomorphism, partly on account of the strong basicity of the lower oxides of these metals, all of which unite directly with water, dissolve in acids with great evolution of heat, and easily form well-crystallised carbonates, all which properties are characteristic of monoxides rather than of sesquioxides.

The following table, taken from Rammelsberg's memoir above cited, exhibits the composition of the naturally occurring compounds (chiefly silicates, niobates, and tantalates) of the cerite and gadolinite metals according to the old and new atomic weights, the symbol R denoting an atom of bivalent metal (Ce = 92; Di = 95; La = 92.5; Eb = 113.7; Y = 59.7), and H an atom of trivalent metal (Ce = 138; Hi = 144; In = 139; Eh = 169; Y = 92.5).

	New.	Old.
Cerite . . .	$R^2Si^2O^{12} + 3aq$	$R^2SiO^4 + 3aq$
Lanthanite . .	$RC^2O^4 + 9aq$	$RCO^3 + 3aq$
Hamartite . .	$\left\{ \begin{array}{l} RF^4 \\ 2HC^2O^3 \end{array} \right\}$	$\left\{ \begin{array}{l} RF^3 \\ 2RCO^3 \end{array} \right\}$
Xenotime . . .	$Y^2P^2O^8 (?)$	$Y^2P^2O^8 (?)$
Cryptolite . .	CeP^2O^8	$Ce^2P^2O^8$
Yttrotantalite .	$\left\{ \begin{array}{l} 5(R^2Ta^2O^7 + 3aq) \\ 2(H^2Ta^2O^7 + 3aq) \end{array} \right\}$	$R^2Ta^2O^7$
	Ta = Ta, Nb	
Fergusonite . .	$\left\{ \begin{array}{l} mR^2Nb^2O^8 + xaq \\ nH^2Nb^2O^8 + xaq \end{array} \right\}$	$R^2Nb^2O^8 + xaq$
	$m : n \quad x(m = n = 1)$ 1 : 5 $\frac{4}{3}$ Greenland, 3 : 4 $\frac{4}{3}$ yellow Yttrotantalite, " : 2 $\frac{4}{3}$ brown-black " 1 : 4 $\frac{7}{3}$ Kärnsfret, 3 : 5 $\frac{4}{3}$ Tyrife, 2 : 3 $\frac{3}{3}$ Ceracite.	
	Nb = Nb and Ta in many cases	
Polycrase . . .	$\left\{ \begin{array}{l} \left\{ \begin{array}{l} RNb^2O^8 \\ nRNb^2O^8 \end{array} \right\} \\ 4 \left\{ \begin{array}{l} RTiO^3 \\ nRTi^2O^8 \end{array} \right\} \end{array} \right\} + xaq$	$\left\{ \begin{array}{l} RNb^2O^8 \\ 4RTiO^3 \end{array} \right\} + xaq$
Crystallised . .	$\frac{n}{2} \quad \frac{x}{18}$	
Massive . . .	$\frac{4}{24}$	
Euxenite . . .	$\left\{ \begin{array}{l} \left\{ \begin{array}{l} mRNb^2O^8 \\ nRNb^2O^8 \end{array} \right\} \\ n \left\{ \begin{array}{l} mRTiO^3 \\ nRTi^2O^8 \end{array} \right\} \end{array} \right\} + xaq$	$\left\{ \begin{array}{l} RnB^2O^8 \\ 2RTiO^3 \end{array} \right\} + xaq$
	$m : n \quad x$ 1 : 4 12 Alyö 4 : 5 30 Mörespär 5 : 4 18 Eydland	
	60NaFl	
Pyrochlore . .	$\left\{ \begin{array}{l} 6 \left\{ \begin{array}{l} 12RNb^2O^8 \\ CeNb^2O^8 \end{array} \right\} \\ 4 \left\{ \begin{array}{l} 12RTiO^3 \\ CeTiO^3 \end{array} \right\} \end{array} \right\}$	$\left\{ \begin{array}{l} 4NaFl \\ 6RNb^2O^8 \\ 4RTiO^3 \end{array} \right\}$
(1) Miask . . .		

CERIUM.

	Ti = Ti and Th.	
	90NaFl	
	$\left. \begin{array}{l} 12\text{RNb}^2\text{O}^6 \\ \text{CeNb}^4\text{O}^{12} \\ 12\text{RTiO}^3 \\ \text{CeTi}^3\text{O}^9 \end{array} \right\}$	
(2) Crevig		$\left\{ \begin{array}{l} 4\text{NaFl} \\ 5\text{RNb}^2\text{O}^6 \\ 2\text{RTiO}^3 \end{array} \right\}$
	Ti = Ti and Th.	
	12NaFl	
	$\left. \begin{array}{l} 20\text{RNb}^2\text{O}^6 \\ \text{CeNb}^4\text{O}^{12} \\ 20\text{RTiO}^3 \\ \text{CeTi}^3\text{O}^9 \end{array} \right\}$	
(3) Fredriksvärn		$\left\{ \begin{array}{l} \text{NaFl} \\ \text{R}^2\text{Nb}^2\text{O}^6 \\ \text{RTiO}^3 \end{array} \right\}$
	21NaFl	
	$\left\{ \begin{array}{l} 10\text{R}^2\text{Nb}^2\text{O}^6 \\ \text{Ce}^2\text{Nb}^4\text{O}^{11} \\ \text{mR}^2\text{SiO}^5 \\ \text{nR}^2\text{SiO}^5 \end{array} \right\}$	
(4) Kaiserstuhl		$\left\{ \begin{array}{l} 5\text{NaFl} \\ 3\text{R}^2\text{Nb}^2\text{O}^6 \\ \text{R}^2\text{SiO}^5 \end{array} \right\}$
Gadolinite		
	$\begin{array}{l} m : n \\ 1 : 1 \text{ Hitteröe} \\ 3 : 2 \text{ Ytterlen} \\ 1 : 3 \text{ " (?) } \\ 5 : 6 \text{ " } \end{array}$	
Orthite	$\left\{ \begin{array}{l} \text{mR}^2\text{SiO}^4 \\ \text{nR}^2\text{Si}^4\text{O}^{12} \end{array} \right\}$	$\left\{ \begin{array}{l} \text{mR}^2\text{SiO}^4 \\ \text{nR}^2\text{Si}^4\text{O}^{12} \end{array} \right\}$
	m : n often = 3 : 2	3 : 1
	Ytrotitanite	
	$\left\{ \begin{array}{l} 3\text{RSiO}^3 \\ 2\text{RTiO}^3 \\ 3\text{RSi}^4\text{O}^9 \\ 2\text{RTi}^3\text{O}^9 \end{array} \right\}$	
	Tschewkinite	
	$\left\{ \begin{array}{l} 3\text{RSiO}^3 \\ 2\text{RTiO}^3 \\ 3\text{RSi}^4\text{O}^9 \\ 2\text{RTi}^3\text{O}^9 \end{array} \right\}$	

Cerium, Ce = 138.* Hillebrand u. Norton (*Pogg. Ann.* clvi. 466) have obtained pure metallic cerium by electrolysis of pure cerous chloride, using an apparatus like those employed for similar purposes by Bunsen and Matthiessen (ii. 437, 438). The metal thus obtained has the colour and lustre of iron, and takes a high polish; in dry air it preserves its lustre, but in moist air it becomes covered with coloured films like heated steel. It is malleable, and when hot can be drawn into wire of remarkable flexibility. Sp. gr. 6.63 to 6.73.† Its melting point is below that of silver, but considerably above that of antimony. It kindles in the air at a lower temperature than is required to ignite magnesium; small fragments inflame by the mere act of detaching them, and showers of brilliant sparks are produced by striking a piece of the metal with a flint. A piece of cerium wire burns with even greater brilliancy than magnesium. Cerium burns in chlorine and in bromine vapour, and combines directly with iodine, sulphur, and phosphorus. Concentrated sulphuric and nitric acids do not attack it in the cold, but these acids, when diluted, dissolve it readily, as does also hydrochloric acid.

Oxides and Salts.—According to the new atomic weight of cerium, the two oxides (formerly CeO^2 and Ce^2O^4) have the formulæ Ce^2O^3 and CeO^3 , the metal in the latter (ceric oxide) being quadrivalent.

Of the salts there are three classes, viz.:

Cerous.
 Ce^2X^2 or CeX^2

Cerous-ceric.
 $\text{CeX}^2.\text{CeX}^4$ or Ce^2X^7

Ceric.
 Ce^2X^4 or CeX^4

* See p. 418. H. Bührig (*J. pr. Chem.* [2], xli. 209), from analyses of cerous oxalate spectroscopically free from didymium, infers that the atomic weight of cerium (diatomic) is 94.1782, which gives for the triatomic metal, 141.2673.

† The lower specific gravity (5.5) of the metal which Wöhler obtained by reducing cerous chloride with sodium (*1st Suppl.* 419) was doubtless due to admixture of sodium.

Of the three sulphates formulated by Rammelsberg, according to the old atomic weight of cerium (2nd Suppl. 275), the brown-red hexagonal salt remains also a ceroso-ceric salt according to the new atomic weight, while the yellow normal ceroso-ceric salt, and the yellow basic salt, become normal and basic ceric salts respectively, thus, (Ce = 92; Ce = 138):

Brown-red Hexagonal Salt, $\left\{ \begin{array}{l} \text{Ce}^2(\text{SO}^4)^2 \\ 2\text{Ce}(\text{SO}^4) \end{array} \right\} + 25\text{aq.}$

Yellow Normal Salt, $\text{Ce}(\text{SO}^4)^2 + 4\text{aq.}$

Yellow Basic Salt (probably), $\left\{ \begin{array}{l} 3\text{Ce}(\text{SO}^4)^2 \\ 5\text{H}^+\text{CeO}^4 \end{array} \right\}$

Crystallised Ammonium Salt, $\left\{ \begin{array}{l} \text{Ce}(\text{SO}^4)^2 \\ 3(\text{NH}^4)^+\text{SO}^4 \end{array} \right\} + 4\text{aq.}$

The following cerous salts have been examined by S. Jolin (*Bull. Soc. Chim.* [2], xxi. 523):—

[Ce = 138.]

Chloride, $\text{CeCl}^3 + 7\text{H}^2\text{O}$.—Large colourless crystals.

Mercurio-chloride, $\text{CeCl}^3.4\text{HgCl}^2 + 10\text{H}^2\text{O}$.—Colourless cubes.

Platinochloride, $\text{CeCl}^3.\text{PtCl}^4 + 13\text{H}^2\text{O}$.—Large orange coloured plates.

Zurochloride, $\text{CeCl}^3.\text{AuCl}^3 + 13\text{H}^2\text{O}$.—Yellow deliquescent prisms.

Bromide, $\text{CeBr}^3 + 11\text{H}^2\text{O}$.—Very deliquescent needles.

Aurobromide, $\text{CeBr}^3.\text{AuBr}^3 + 8\text{H}^2\text{O}$.—Dark brown, shining crystals.

Fluoride, $2\text{CeF}^3 + \text{H}^2\text{O}$.—Gelatinous precipitate.

Thiocyanate, $\text{Ce}(\text{CNS})^3 + 7\text{H}^2\text{O}$.—Colourless prisms.

$\text{Ce}(\text{CNS})^3.3\text{Hg}(\text{CN})^2 + 12\text{H}^2\text{O}$.—Well-defined tabular crystals.

Ceroseo-potassic Ferrocyanide, $\left\{ \begin{array}{l} \text{Ce} \\ \text{K} \end{array} \right\} (\text{CN})^4\text{Fe} + 3\text{H}^2\text{O}$.—White powder.

Cerous Ferrocyanide, $\text{Ce}^2(\text{CN})^7\text{Fe} + 8\text{H}^2\text{O}$.

Ceroseo-platinous Cyanide, $2\text{Ce}(\text{CN})^3.3\text{Pt}(\text{CN})^2 + 18\text{H}^2\text{O}$.—Yellow-green prisms.

Nitrate, $\text{Ce}(\text{NO}^3)^3 + 6\text{H}^2\text{O}$.

Chlorate, $\text{Ce}(\text{ClO}^3)^3 + 8\text{H}^2\text{O}$.

Iodate, $\text{Ce}(\text{IO}^3)^3 + 2\text{H}^2\text{O}$.—White amorphous precipitate.

Sulphate, $\text{Ce}^2(\text{SO}^4)^2 + 5, 6, 8, 9 \text{ and } 12\text{H}^2\text{O}$.

Ceroseo-potassic Sulphate, $\text{Ce}^2(\text{SO}^4)^2.2\text{K}^2\text{SO}^4 + 2\text{H}^2\text{O}$.

Ceroseo-ammoniac Sulphate, $\text{Ce}^2(\text{SO}^4)^2.(\text{NH}^4)^2\text{SO}^4 + 8\text{H}^2\text{O}$.—Flattened prisms.

Ceroseo-sodic Sulphate, $\text{Ce}^2(\text{SO}^4)^2.\text{Na}^2\text{SO}^4 + 2\text{H}^2\text{O}$.—White crystalline powder.

Selenate, $\text{Ce}^2(\text{SeO}^4)^2 + 6, 9, \text{ and } 12\text{H}^2\text{O}$.

Ceroseo-potassic Selenate, $\text{Ce}^2(\text{SeO}^4)^2.5\text{K}^2\text{SeO}^4$.

Ceroseo-ammoniac Selenate, $\text{Ce}^2(\text{SeO}^4)^2.(\text{NH}^4)^2\text{SeO}^4 + 9\text{H}^2\text{O}$.—Small, well-defined prisms.

Ceroseo-sodic Selenite, $\text{Ce}^2(\text{SeO}^3)^2.\text{Na}^2\text{SeO}^3 + 5 \text{ (or } 4?) \text{ H}^2\text{O}$.—Small colourless crystals.

Selenite, $\text{Ce}^2(\text{SeO}^3)^2 + 3\text{H}^2\text{O}$.

Ceroseo-hydric Selenite, $\text{CeH}(\text{SeO}^3)^2 + 2\text{H}^2\text{O}$.

Dithionate, $\text{Ce}^2(\text{S}^2\text{O}^6)^2 + 24\text{H}^2\text{O}$.—Large hexagonal crystals.

Sulphite, $\text{Ce}^2(\text{SO}^3)^2 + 3\text{H}^2\text{O}$.

Carbonate, $\text{Ce}^2(\text{CO}^3)^2 + 5\text{H}^2\text{O}$.

Ceroseo-potassic Carbonate, $\text{Ce}^2(\text{CO}^3)^2.\text{K}^2\text{CO}^3 + 3\text{H}^2\text{O}$.

Ceroseo-sodic Carbonate, $\text{Ce}^2(\text{CO}^3)^2.2\text{Na}^2\text{CO}^3 + 2\text{H}^2\text{O}$.

Cerous Phosphate, $\text{CePO}^4 + 2\text{H}^2\text{O}$.

Ceroseo-hydric Pyrophosphate, $\text{CeHP}^2\text{O}^7 + 3\text{H}^2\text{O}$.

Formate, $\text{Ce}(\text{CO}^2\text{H})^3$.

Acetate, $2\text{Ce}(\text{C}^2\text{H}^3\text{O}^2)^2 + 3\text{H}^2\text{O}$.—Small flexible needles.

Oxalate, $\text{Ce}^2(\text{C}^2\text{O}^4)^2 + 9\text{H}^2\text{O}$.

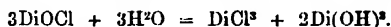
Lanthanum, La''' = 139. Metallic lanthanum has been prepared by Hillebrand & Norton, in the same manner as cerium, viz. by electrolytic reduction from the chloride. In its general chemical behaviour, it resembles cerium; it is, however, readily attacked by strong nitric acid, and quickly becomes covered with a steel-blue film even in dry air. It is malleable, but not ductile. The sp. gr. of the electrolytically deposited metal is 6.163; after fusion, 6.049. Its melting point appears to be not far from that of cerium, but its temperature of ignition both in air and in oxygen is much higher than that of cerium.

CERITE METALS (LANTHANUM).

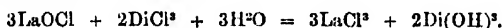
Atomic Weights.—Marignac (*Ann. Ch. Phys.* [4], xxx. 67) by igniting lanthanum sulphate till the sulphuric acid is completely expelled, finds the atomic weight to be: $\text{La} = 92.52$; and by precipitation with ammonium oxalate and ignition of the precipitate, $\text{La}'' = 92.24$ and 92.48 . The most probable value deduced from these numbers is 92.5 , or for the triatomic metal, $\text{La}''' = 138.75$.

Cleve (*Bull. Soc. Chim.* [2], xxi. 196) has determined the atomic weight of lanthanum by converting the oxide (spectroscopically pure) into sulphate. The maximum number thus obtained was 139.49 ; minimum, 138.95 ; mean, 139.15 . Comparing this with Marignac's number, the true atomic weight of lanthanum may be taken at 139 .

Separation from Didymium.—According to Cleve (*loc. cit.*) the separation is best effected by fractional precipitation of the mixed nitrates with ammonia. The precipitate consists chiefly of basic didymium nitrate, and by repeated fractionation, a solution of pure lanthanum nitrate is obtained, which may be precipitated by oxalic acid. The following methods are given by Frerichs (*Deut. Chem. Ges. Ber.* vii. 798).
1. The oxides of the two metals are ignited in chlorine gas, whereby they are converted into the oxychlorides, LaOCl and DiOCl . The oxychloride of lanthanum is not altered by boiling with water, whereas that of didymium is resolved thereby into chloride and hydroxide:



Moreover, didymium chloride and lanthanum oxychloride act on one another, as shown by the equation:



If, therefore, the proportion of lanthanum in the original mixture of the oxides was such that 3 atoms of lanthanum can enter into the reaction with every 6 atoms of didymium (or 1La to 2Di), the mixture, after several days' digestion will contain nothing but lanthanum chloride, and the precipitate will consist of didymium hydroxide and lanthanum oxychloride; but if a larger proportion of didymium is present, the product will contain didymium chloride, and must be again treated in the same way.

2. If the amount of lanthanum in the mixed oxides is known, the oxides may be dissolved in nitric acid, and exactly enough sulphuric acid added to convert the lanthanum nitrate into sulphate. The solution is then evaporated to dryness, and the salts heated to low redness to decompose the didymium nitrate. The lanthanum sulphate is then extracted with water, leaving didymium oxide undissolved. If a slight excess of sulphuric acid be added, so that a portion of the didymium nitrate is also converted into sulphate, the insoluble residue will consist of pure didymium oxide.

COMPOUNDS OF LANTHANUM.—The following have been prepared and analysed by Cleve (*loc. cit.*)

Oxide, La_2O_3 .—This is the only known oxide of lanthanum. After ignition at a white heat it has a sp. gr. of 6.53 at 17° . Moistened with warm water it evolves considerable heat, and the hydrate, dried at 100° , has the formula LaH_2O^4 .

Chloride of Lanthanum (hydrated), $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$.—Colourless prisms, very soluble in water and alcohol. Hermann assigns only $6\text{H}_2\text{O}$ to this salt. The bromide resembles the chloride.

Oxychloride, LaOCl , prepared by heating the oxide to 200° in chlorine gas, is a grey mass scarcely attacked by water (Frerichs).

Platinochloride, $\text{LaCl}_3 \cdot \text{PtCl}_4 \cdot 13\text{H}_2\text{O}$.—Large, square plates, very soluble. It loses $5\text{H}_2\text{O}$ over sulphuric acid, and $9\text{H}_2\text{O}$ at 100° – 110° .

Aurochloride, $\text{LaCl}_3 \cdot \text{AuCl}_3 \cdot 10\text{H}_2\text{O}$.—Loses $4\text{H}_2\text{O}$ over sulphuric acid.

Aurobromide, $\text{LaBr}_3 \cdot \text{AuBr}_3 \cdot 9\text{H}_2\text{O}$ (possibly $10\text{H}_2\text{O}$).—Permanent over sulphuric acid.

Fluoride, $2\text{LaF}_3 \cdot \text{H}_2\text{O}$ (?).—Gelatinous precipitate produced by the addition of hydrofluoric acid to the acetate.

Ferrocyanide of Lanthanum and Potassium, $\text{La}''\text{KFeCy}_6 \cdot 4\text{H}_2\text{O}$.—A yellowish white precipitate, formed on adding ferrocyanide of potassium to acetate of lanthanum. It loses H_2O at 100° .

Platinocyanide, $2\text{LaCy}_3 \cdot 3\text{PtCy}_2 \cdot 18\text{H}_2\text{O}$.—Forms greenish-yellow prisms; loses $13\text{H}_2\text{O}$ over sulphuric acid, and $14\text{H}_2\text{O}$ at 100° – 110° .

Thiocyanate, $\text{La(CNS)}_3 \cdot 7\text{H}_2\text{O}$.—Obtained by dissolving the oxide in thiocyanic acid. It forms deliquescent needles, which lose $3\text{H}_2\text{O}$ over sulphuric acid; gives with mercuric cyanide the compound $\text{La(CNS)}_3 \cdot 3\text{Hg(CN)}_2 \cdot 12\text{H}_2\text{O}$, which separates in white

scales. It is very soluble in hot water, only slightly so in cold water, loses $6\text{H}_2\text{O}$ over sulphuric acid, and all its water at 110° .

Nitrate, $\text{La}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$.—Large tabular crystals, losing $2\frac{1}{2}\text{H}_2\text{O}$ over sulphuric acid.

Chlorate.—Colourless needles, very deliquescent. Its solution is decomposed by evaporation in a vacuum.

Perchlorate, $\text{La}(\text{ClO}_4)_3 + 18\text{H}_2\text{O}$.—Colourless, deliquescent needles.

Iodate, $\text{La}(\text{IO}_3)_3 + 3\text{H}_2\text{O}$.—Voluminous white precipitate, devoid of crystalline appearance, obtained on adding iodic acid to a lanthanum salt.

Periodate, $\text{LaIO}_3 + 2\text{H}_2\text{O}$.—Periodic acid does not precipitate the nitrate, but with the acetate it gives a bulky white precipitate, which shrinks on gently warming.

Formate, $(\text{CO}_2\text{H})_3\text{La}$.—White crystalline powder, which requires 421 parts of cold water for solution. The formates of cerium and didymium have a similar slight solubility, while those of yttrium and erbium are very soluble.

Acetate, $2(\text{C}_2\text{H}_3\text{O}_2)_3\text{La} + 3\text{H}_2\text{O}$.—Crystallises in small needles, which lose $1\text{H}_2\text{O}$ at 100° – 110° .

Selenate, $\text{La}_2(\text{SeO}_4)_3 + 6\text{H}_2\text{O}$, when crystallised from a warm solution, and with $4\text{H}_2\text{O}$ by spontaneous evaporation.

Lanthano-potassic Sulphate, precipitated on mixing solutions of the two sulphates, is completely insoluble in a concentrated solution of potassium sulphate.

Lanthano-potassic Selenate, $(\text{SeO}_4)_2\text{La}_2\text{SeO}_4\text{K}_2 + 9\text{H}_2\text{O}$, obtained by evaporating a mixture of the two selenates, does not give off water in dry air.

Lanthanumammonic Sulphate, $(\text{SO}_4)_2\text{La}_2\text{SO}_4(\text{NH}_4)_2 + 8\text{H}_2\text{O}$.—Flattened striated prisms, very soluble, permanent in the air.

Lanthanumammonic Selenate, $(\text{SeO}_4)_2\text{La}_2\text{SeO}_4(\text{NH}_4)_2 + 8\text{H}_2\text{O}$.—Flattened prisms, giving off $7\text{H}_2\text{O}$ over sulphuric acid, and $8\text{H}_2\text{O}$ at 100° .

Lanthano-sodic Sulphate, $(\text{SO}_4)_2\text{La}_2\text{SO}_4\text{Na}_2 + 3\text{H}_2\text{O}$.—White amorphous powder, slightly soluble.

Lanthano-sodic Selenate, $(\text{SeO}_4)_2\text{La}_2\text{SeO}_4\text{Na}_2 + 4\text{H}_2\text{O}$.—White crystalline crusts, moderately soluble. It loses nothing in a vacuum over sulphuric acid.

Sulphite of Lanthanum, $(\text{SO}_3)_2\text{La}_2 + 4\text{H}_2\text{O}$.—Hydrate of lanthanum dissolves in a solution of sulphurous acid. The above salt separates on heating, as a bulky white powder.

Acid Selenite, $(\text{SeO}_3)_2\text{La}_2\text{SeO}_3 + 5\text{H}_2\text{O}$.—Separates from a mixture of lanthanum chloride with selenious acid on addition of alcohol. It loses $3\text{H}_2\text{O}$ at 100° .

Dithionate, $(\text{S}_2\text{O}_8)_2\text{La}_2 + 2\text{H}_2\text{O}$.—Prepared by double decomposition between barium dithionate and lanthanum sulphate. It forms hexagonal crystals, is very soluble, and loses $23\text{H}_2\text{O}$ over sulphuric acid.

Carbonate.—The rare mineral *lanthanite* has the formula $(\text{CO}_3)_2\text{La}_2 + 8\text{H}_2\text{O}$.—The salt obtained by precipitating a lanthanum salt with an alkaline carbonate has the same composition. By passing carbonic acid through water holding lanthanum hydrate in suspension, a carbonate is obtained in small scales with greasy lustre, which when dried in a vacuum has the composition $(\text{CO}_3)_2\text{La}_2 + 3\text{H}_2\text{O}$.

Fluo-carbonate.—The mineral *harmatite* found at Bastnäs (Sweden) has, according to Nordenskiöld, the composition $\text{La}(\text{Co})\left\{\begin{smallmatrix} \text{F} \\ \text{O}_2\text{CO} \end{smallmatrix}\right.$. Unlike didymium, lanthanum does not appear to form double carbonates with the alkalis.

Oxalate, $(\text{C}_2\text{O}_4)_2\text{La}_2 + 9\text{H}_2\text{O}$.—White crystalline powder completely insoluble in water, very soluble in strong nitric acid, slightly soluble in dilute hydrochloric.

Succinate, $(\text{C}_4\text{H}_4\text{O}_4)_2\text{La}_2 + 5\text{H}_2\text{O}$.—Czudnowicz assigned $4\frac{1}{2}\text{H}_2\text{O}$ to this salt, but his analyses agree better with the formula above given.

Tartrate, $(\text{C}_4\text{H}_4\text{O}_6)_2\text{La}_2 + 3\text{H}_2\text{O}$.—The addition of tartaric acid to a solution of lanthanum acetate produces a bulky precipitate, which slowly becomes granular. It is soluble in acids, and the solutions are not precipitated by ammonia.

Orthophosphate.—Disodic orthophosphate and phosphoric acid produce precipitates in lanthanum solutions.

Acid Pyrophosphate, $\text{P}_2\text{O}_7\text{HLa} + 3\text{H}_2\text{O}$.—Sodium pyrophosphate gives with solution of lanthanum chloride a precipitate soluble in excess of the lanthanum salt. This solution deposits after some days small crystalline grains of the above composition. It loses $2\text{H}_2\text{O}$ at 100° .

On reviewing the composition of these salts, it will be seen that the platino-chloride, aurochloride, aurobromide, potassio-ferrocyanide, pyrophosphate, and bar-

matite afford the strongest evidence in favour of the triatomicity of lanthanum. The formulæ of the double sulphates and selenates, the quantity of water in the crystalline salts, and the proportion of it given off under various circumstances, likewise all agree best with this view.

Didymium, $\text{Di}''' = 145$. Cleve (*Bull. Soc. Chim.* [2], xxi, 246) has determined the atomic weight of this metal in the same manner as that of lanthanum. A pure basic nitrate obtained by fractional precipitation with ammonia, was converted into the formate, which on calcination left the pure sesquioxide Di_2O_3 . The conversion of this oxide into the sulphate gave, as a mean of six determinations, $\text{Di} = 147.01$ (extremes 147.23 and 146.65), Marignac found 143.6 to 144.

Metallic didymium has a greater resemblance to lanthanum than to cerium. It resembles lanthanum in its chemical relations, and is also about equal to it in lustre, ductility, and susceptibility of polishing. Its colour is white with a tinge of yellow, but much less marked than in bismuth: it tarnishes in dry air, and when exposed to moist air acquires a yellowish coating. After fusion it has a sp. gr. of 6.544, and is but little inferior in hardness to cerium. Fine particles thrown off in scraping or scratching it do not take fire spontaneously, but burn with great brilliancy when thrown into a flame. Light reflected from polished surfaces of the metal does not exhibit the absorption-bands which are seen in the spectrum of the incandescent oxide.

The following didymium compounds have been examined by Cleve:

Oxide of Didymium, Di_2O_3 , is obtained in hard fragments of a dirty bluish colour and with a sp. gr. of 6.852, by igniting the hydrate at a white heat. The peroxide obtained by calcining the oxalate becomes bluish when ignited in hydrogen.

Chloride, $\text{DiCl}_3 + 6\text{H}_2\text{O}$.—Unalterable in dry air. Marignac found the same composition, but Zschiesche assigns more water to this salt.

Bromide, $\text{DiBr}_3 + 6\text{H}_2\text{O}$.—Crystallises in large prisms of a deep violet colour. It is not altered by exposure to dry air.

Platinochloride, $\text{DiCl}_3 \cdot \text{PtCl}_4 + 11\text{H}_2\text{O}$.—Crystallises over sulphuric acid in orange-coloured prisms, which are not isomorphous with the platinochlorides of lanthanum and cerium. Marignac has described a platinochloride having the formula $4\text{Di}'''\text{Cl}_3 \cdot 3\text{PtCl}_4 + 36\text{H}_2\text{O}$, isomorphous with those of lanthanum and cerium. The two are evidently distinct compounds.

Aurochlorides.—(a.) $\text{DiCl}_3 \cdot \text{AuCl}_3 + 10\text{H}_2\text{O}$.—Large orange-coloured plates, very soluble. It loses $3\text{H}_2\text{O}$ over sulphuric acid.

(b.) $2\text{DiCl}_3 \cdot 3\text{AuCl}_3 + 20(?)\text{H}_2\text{O}$. Obtained on one occasion of a deeper colour than the preceding.

Aurobromide, $\text{DiBr}_3 \cdot \text{AuBr}_3 + 9(?)\text{H}_2\text{O}$.—Large crystals of a deep-brown colour, very soluble; loses $4\text{H}_2\text{O}$ over sulphuric acid.

Fluoride, $\text{DiF}_3 + \text{H}_2\text{O}(?)$.—Gelatinous precipitate.

Platinocyanide, $2\text{Di}(\text{CN})_3 \cdot 3\text{Pt}(\text{CN})_6 + 18\text{H}_2\text{O}$.—Fine prisms, of a dirty yellow colour, with bluish reflex; loses $14\text{H}_2\text{O}$ on exposure to air, becoming first red, then yellow or white; parts with the same quantity of water at 100° .

Didymio-potassic Ferrocyanide, $\left\{ \begin{smallmatrix} \text{Di} \\ \text{K} \end{smallmatrix} \right\} \text{FeCy}_6 + 4\text{H}_2\text{O}(?)$.—White precipitate formed on adding potassium ferrocyanide to a didymium salt.

Thiocyanate of Didymium, $\text{Di}(\text{CSN})_3 + 6\text{H}_2\text{O}$.—Deliquescent needles, very soluble. It loses $2\text{H}_2\text{O}$ over sulphuric acid. With mercuric cyanide it forms the compound $\text{Di}(\text{CSN})_3 \cdot 3\text{Hg}(\text{CN})_2 + 12\text{H}_2\text{O}$, which crystallises in pale rose-coloured needles, very soluble in hot water, but only slightly so in cold. It loses $7\text{H}_2\text{O}$ over sulphuric acid and $10\text{H}_2\text{O}$ at 100° .

Nitrate, $\text{Di}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$.—Large violet crystals.

Perehlorate, $\text{Di}(\text{ClO}_4)_3 + 9\text{H}_2\text{O}$.—Red needles, very deliquescent.

Iodate, $\text{Di}(\text{IO}_3)_3 + 2\text{H}_2\text{O}$.—Non-crystalline, white precipitate, obtained by adding iodic acid to a didymium salt.

Periodate, $\text{DiIO}_3 + 4\text{H}_2\text{O}$.—Periodic acid gives no precipitate with didymium nitrate, but on adding a little ammonia, there is obtained a bulky precipitate, which soon changes to a reddish crystalline powder.

Formate, $\text{Di}(\text{CO}_2\text{H})_3$.—Red crystalline powder, obtained by treating didymium hydrate with formic acid or by precipitating a didymium salt with ammonium formate: dissolves in 221 parts of cold water.

Acetate, $\text{Di}(\text{C}^2\text{H}_3\text{O}_2)_3 + 8\text{H}_2\text{O}$.—Isomorphous with the acetates of erbium and yttrium.

Selenates. (a) $\text{Di}^2(\text{SeO}_4)^2 + 5\text{H}_2\text{O}$.—Fine red needles, obtained by evaporating on the water-bath a solution of didymium oxide in selenic acid. (b) $\text{Di}^2(\text{SeO}_4)^2 + 8\text{H}_2\text{O}$. Large crystals, very soluble, isomorphous with the sulphate, obtained by evaporation at 60° . (c). Evaporation at the ordinary temperature gives needles which appear to contain $10\text{H}_2\text{O}$.

Didymio-potassic Sulphates. (a) $\text{Di}^2(\text{SO}_4)^2 \cdot 3\text{K}^2\text{SO}_4$.—A red crystalline powder, which separates on mixing the cold saturated solutions of the two sulphates. It is absolutely insoluble in a cold saturated solution of potassium sulphate, but dissolves to a small extent on boiling (100 c.c. contain 55 mgr. Di^2O^2). It dissolves in about 83 parts of pure water at 18° . (b). The mixture of boiling solutions of the sulphates gives a salt whose formula appears to be $\text{Di}^2(\text{SO}_4)^2 + 4\text{K}^2\text{SO}_4$.

Didymio-potassic Selenates. $\text{Di}^2(\text{SeO}_4)^2 \cdot \text{K}^2\text{SeO}_4 + 9\text{H}_2\text{O}$.—Obtained in small crystals by spontaneous evaporation. Permanent in the air; loses $6\text{H}_2\text{O}$ at 100° .

Didymio-ammonic Sulphate. $\text{Di}^2(\text{SO}_4)^2 \cdot (\text{NH}_4)^2\text{SO}_4 + 7\text{H}_2\text{O}$.—Loses $6\text{H}_2\text{O}$ at 100° .

Didymio-ammonic Selenate. $\text{Di}^2(\text{SeO}_4)^2 \cdot (\text{NH}_4)^2\text{SeO}_4 + 6\text{H}_2\text{O}$.—Flattened prisms, very soluble.

Didymio-sodic Sulphate. $\text{Di}^2(\text{SO}_4)^2 \cdot \text{Na}^2\text{SO}_4 + 2\text{H}_2\text{O}$.—Red powder, of slight solubility.

Didymio-sodic Selenate. $\text{Di}^2(\text{SeO}_4)^2 \cdot \text{Na}^2\text{SeO}_4 + 4\text{H}_2\text{O}$.—Resembles the last salt, but is much more soluble.

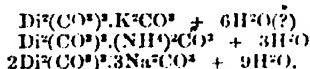
Sulphite of Didymium. $\text{Di}^2(\text{SO}_3)^2 + 3\text{H}_2\text{O}$.—A nearly white crystalline powder precipitated on heating the reddish solution of the hydrate in sulphurous acid.

Selenite. $\text{Di}^2(\text{SeO}_3)^2 \cdot \text{SeO}_3 + 4\text{H}_2\text{O}$.—Separates from a mixture of didymium nitrate with selenious acid on addition of alcohol. It loses $2\text{H}_2\text{O}$ at 100° .

Dithionate. $\text{Di}^2(\text{S}_2\text{O}_8)^2 + 24\text{H}_2\text{O}$.—Hexagonal crystals, very soluble, of a fine red colour. It loses $20\text{H}_2\text{O}$ over sulphuric acid.

Carbonate. $\text{Di}^2(\text{CO}_3)^2 + \text{H}_2\text{O}$.—Red crystalline powder obtained by passing carbonic acid into water holding in suspension hydrate of didymium.

Double Carbonates.—



Obtained by adding a salt of didymium to an excess of the alkaline carbonate.

$\text{Di}^2(\text{CO}_3)^2 \cdot 2\text{Na}^2\text{CO}_3 + 8\text{H}_2\text{O}$.—Obtained once by digestion of didymium carbonate with an excess of sodium carbonate at a gentle heat.

Oxalate of Didymium. $\text{Di}^2(\text{C}_2\text{O}_4)^2 + 10\text{H}_2\text{O}$.—Crystalline powder.

Oxalate of Didymium and Potassium. $\text{Di}^2(\text{C}_2\text{O}_4)^2 \cdot \text{K}^2\text{C}_2\text{O}_4 + 4\text{H}_2\text{O} (?)$.—Oxalate of didymium dissolves in a boiling saturated solution of potassium oxalate; on diluting this solution the double salt separates as a bulky precipitate, speedily becoming crystalline.

Tartrate of Didymium. $\text{Di}^2(\text{C}_4\text{H}_4\text{O}_6)^2 + 6\text{H}_2\text{O}$.—Tartaric acid gives a red granular precipitate with didymium acetate. It loses $4\text{H}_2\text{O}$ at 100° – 110° . It is soluble in ammonia, and the solution yields yellow transparent masses like gum.

Pyrophosphate of Didymium. $\text{Di}^2(\text{P}_2\text{O}_7)^2 + 8\text{H}_2\text{O}$.—Bulky red precipitate.

CERUSSITE. This mineral was observed by N. v. Kokscharow to form two kinds of twin-crystals, namely, the ordinary form in which the combination-face is parallel to ∞P , and another in which it is parallel to ∞P_3 . Crystals of the latter kind were found in the Soltau-Schinsk mine in the Altai mountains, and Schrauf (*Jahrb. f. Min.* 1874, 306) has found that crystals formed according to the same law occur at two other localities, namely, Rezbanya in Hungary, and Leadhills in Scotland. Those from the last-named locality show distinctly, by their mode of development, that cerussite twins having their face of combination parallel to ∞P_3 are hemitropic.

CHALKOSIDERITE. A mineral first described by Ullmann as occurring in the form of a thin crystalline coating, investing the green iron ore (dufrenoyite) of the Hollerter Zug, Sayn, Westphalia, and more recently by Maskelyne (*Chem. Soc. J.* 1876, 580), as associated with andrewsite (p. 84), sometimes standing out from the globules of the latter in bright green crystals, sometimes encrusting the andrewsite with a thin surface-layer. The crystals are triclinic, the ratio of the three axes being:

$$a : b : c = 1 : 0.7907 : 0.60478$$

and their angles of inclination:

$$ab = 107^\circ 41'; ac = 92^\circ 50'; bc = 93^\circ 30'.$$

Sp. gr. = 3.108 approximately. Hardness = 4.5. Streak light siskin-green. An analysis by Flight gave :

Fe ² O ³	Al ² O ³	CaO	P ² O ⁵	As ² O ³	H ² O	UO ²
42.81	4.45	8.15	29.93	0.61	15.00	trace = 100.95

which may be represented by the formula $2\text{Fe}^2\text{P}^2\text{O}^5.\text{Fe}^3\text{H}^4\text{O}^6.\text{CaH}^2\text{O}^2 + 4\text{H}^2\text{O}$. Of the water only 0.468 goes off at 100°, and 0.131 at 120°-130°, the rest being expelled only at a high temperature.

CHEMICAL ACTION. The second part of Brodie's 'Calculus of Chemical Operations,' entitled 'On the Analyses of Chemical Events,' is published in the *Philosophical Transactions* for 1877, vol. clxvii. pp. 36-116; abstr. *Proc. Roy. Soc.* xxv. 83.

E. J. Mills has published *Considerations on the First Principles of Chemistry*, in which Motion is regarded as the groundwork of chemical action (*Phil. Mag.* [5], i. 1-16).

A theory of Chemical Affinity, with special reference to the constitution of Molecular Compounds, and the number of possible Isomeric modifications of compounds, has been proposed by H. Kommrath (*Deut. Chem. Ges. Ber.* ix. 1392; x. 742).

Velocity of Chemical Action. Observations on the time occupied in the double decomposition of salts have been made by J. H. Gladstone (*Chem. News*, xxxi. 266). Ferric chloride and potassium thiocyanate react instantaneously; between ferric citrate and meconic acid, and between platinic chloride and potassium chloride, the reaction is gradual. The progress of the reaction depends upon the rapidity of interdiffusion of the salts, and is greatly influenced by temperature. The following numbers exhibit the rate of precipitation of strontium sulphate by addition of calcium sulphate to a solution of strontium nitrate :

After 4 minutes	Turbidity
20	0.071 grm.
60	0.130 "
110	0.303 "
270	0.497 "
1270	0.659 "
Total precipitation possible.	1.5 "

Marie F. Reed (*American Chemist*, v. 358) has determined the influence of temperature on the rate of the reaction between oxalic acid and potassium permanganate. The mode of experiment consisted in suddenly arresting the action by adding an excess of potassium iodide, and determining the amount of free iodine by means of sodium thiosulphate, whence the quantity of unreduced permanganate could be calculated. In the first five experiments the solutions of oxalic acid and permanganate used were decinormal, and the quantities taken were 25 c.c. permanganate, 50 c.c. oxalic acid, and 2.5 c.c. sulphuric acid of sp. gr. 1.8. In experiments 6, 7 and 8, the solution contained per litre, 32.4 grams of oxalic acid, 17.6 of sulphuric acid, 5 of manganous sulphate, and 0.375 of permanganate, and the quantity taken of each was 25 c.c.

Amount per cent. of Reaction at different Temperatures.

Temperature	1 min.	2 min.	3 min.	4 min.	5 min.	6 min.	7 min.	8 min.
5°	—	—	—	—	—	3	4	4
10	—	—	—	—	—	3.5	4.6	5
15	—	—	3	6	9	5	8	9.5
20	—	—	3.5	6.5	11.5	8.7	15.5	19
25	—	—	3.8	8	13.5	17	33	40
30	—	—	4.9	10	18.5	36	58	65.5
35	—	2.5	7	16.5	42	62.5	78.5	84.5
40	2.5	7.5	16.5	35	97.5	84.5	93	97.5
45	4.5	14.5	33.5	90.5	—	97.5	—	—
50	10	25	70	—	—	—	—	—
55	19	53	98.5	—	—	—	—	—
60	34.5	89.5	—	—	—	—	—	—
65	68	—	—	—	—	—	—	—
70	97	—	—	—	—	—	—	—

Rate of Decomposition of Calcium Carbonate by Acids.—From experiments by Boguski (*Deut. Chem. Ges. Ber.* ix. 1846), it appears that the rapidity of evolution of carbon dioxide from Carrara marble by the action of hydrochloric acid is directly proportional to the concentration of the acid; and further experiments by Boguski and Kajander (*ibid.* 1809) have shown that the quantities of CO_2 expelled in a unit of time from the same marble by the action of nitric, hydrobromic, and hydrochloric acids, are inversely proportional to the molecular weights of these acids. Experiments with acetic and formic acid did not lead to any definite result, inasmuch as these acids alter the surface of the marble.

Retardation of Chemical Reactions by Indifferent Substances. A mixture of equal volumes of fuming hydrochloric acid and glycerin (a) acts on ultramarine only after 45 seconds, and bleaches it in 3 minutes, while a mixture of equal volumes of water and acid (b) begins to act in 10 seconds and destroys the colour in 35 seconds. Mixture a dissolves zinc and iron much more slowly than b. Thus 10 c.c. of the latter dissolved 0.5 gram of nails in less than 24 hours, while a left after 24 hours 86.2 per cent. undissolved, and after 14 days 1.3 per cent. still remained. The cause of this is not that ferrous chloride is less soluble in glycerin than in water, because the salt readily dissolves in the former, and during the experiment none separated out. Mixtures of sulphuric acid and glycerin, or gum, show a similar inactivity. A mixture of acid and soot scarcely acts on metals, but on removing the soot by filtration the filtrate acts like fresh acid. The retardation reaches a maximum when a mixture of strong acid and glycerin with 5 per cent. of soot is used (G. Lunge, *Deut. Chem. Ges. Ber.* ix. 1315).

Decomposition of certain Salts by Water (A. Ditte, *Compt. rend.* lxxix. 915, 1254). Normal Mercuric Sulphate, HgSO_4 or $\text{HgO} \cdot \text{SO}_3$, is decomposed by water at 12° , with separation of basic sulphate or turpeth-mineral, $3\text{HgO} \cdot \text{SO}_3$, till a solution is formed containing 67 grams of free sulphuric acid in a litre, from which point the neutral sulphate is dissolved without decomposition. At higher temperatures, however, the solution again attacks the neutral salt and acquires a yellow colour. The result is not altered by the presence of another acid.

Crystals of normal bismuth nitrate, $2\text{Bi}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ or $\text{Bi}_2\text{O}_3 \cdot 3\text{N}^{70}_3 + 3\text{H}_2\text{O}$, are decomposed by water, with formation of a crystalline precipitate having the composition $\text{Bi}_2\text{O}_3 \cdot \text{N}^{70}_3$, with 1, 2, 3, or 4 mol. water, according to the temperature, until a solution is formed containing 83 grams of nitric anhydride in a litre, after which the normal nitrate is dissolved without decomposition. But if an acid liquid containing less than 83 grams per litre be poured upon the basic nitrate, the latter dissolves as such, and it is not until the limiting quantity of free acid has been otherwise introduced into the solution, that the sense of the reaction is changed, or that the solution becomes capable of dissolving the neutral salt without decomposing it.

The quantity of free acid required increases with the temperature, so that when a solution of the neutral salt is heated, a precipitate of basic nitrate is produced.

The crystalline basic nitrate, $\text{Bi}_2\text{O}_3 \cdot \text{N}^{70}_3$ or $\text{BiO} \cdot \text{NO}_3$, is in its turn capable of being decomposed by a large quantity of water, and a still more basic salt produced, which is amorphous and opaque. This secondary action is very slight at ordinary temperatures, and does not in any way affect the preceding observations, but at 100° the limiting quantity of acid required to prevent decomposition appears to be about 4.5 grams per litre. Protracted washing of the basic nitrate finally leaves a salt of fixed composition, $2[\text{BiO}(\text{NO}_3)]_2 \cdot \text{Bi}_2\text{O}_3$.

Antimonious chloride, SbCl_3 , is decomposed by water, with separation of oxychloride, SbOCl , till a solution is formed containing 150 grams of HCl in a litre, after which it dissolves without decomposition. Antimony oxychloride is decomposed by water, especially at 100° .

The decomposition of bismuth trichloride by different quantities of water has been studied by W. Ostwald (*J. pr. Chem.* xii. 264). A pure concentrated solution of this compound in hydrochloric acid was divided into 25 parts, each of these diluted with a different quantity of water, and after six weeks' rest, the clear liquids were analysed. The action was found to have taken place as represented by the equation $\text{BiCl}_3 + \text{H}_2\text{O} = \text{BiOCl} + 2\text{HCl}$. For 3 to 12 per cent., but not for less than 3 per cent. of bismuth, the following law holds good: When a hydrochloric solution of bismuth is partially decomposed by water, the water withdraws from the bismuth chloride a quantity of chlorine proportional to its own quantity, in the form of hydrochloric acid, and in such a manner that the formation of this constant compound of hydrogen chloride and water is accompanied by the formation of a compound, likewise constant, of hydrogen chloride and bismuth chloride; the proportion of these two double compounds one to the other may however be very variable. Since now, according to this simple law, the action is proportional to the mass, it follows that when a concentrated solution of bismuth in hydrochloric acid is mixed, one time

with a small and another time with a large quantity of water, the mixture of the liquids filtered after standing for some time will neither become turbid nor dissolve oxychloride added to it.

On the Decomposition of Potassio-calcio sulphate by water, see Ditte (*Compt. rend.* lxxix. 1254).

Double Decomposition of Salts in Solution. From the experiments of Joulin (*Ann. Chim. Phys.* [4], xxx. 248), it appears that the reaction between the carbonates of the alkali-metals and salts of the heavy metals, whether the corresponding oxides are capable or not of forming hydrates, results in the formation of mixtures of carbonate and oxide, usually in indefinite proportions, and at every degree of dilution if the alkaline carbonate is in excess, but only up to a certain degree of dilution if the heavy metallic salt is in excess. The course of the reaction is retarded by dilution, and by an excess of either of the salts. A secondary action takes place at the same time, consisting in a decomposition of the metallic carbonate by the still undecomposed alkaline carbonate. Neutral manganous phosphate remains unaltered under water or under a concentrated solution of acid sodium phosphate, but is altered to a very slight extent under a solution of neutral phosphate, and is immediately decomposed by the basic phosphate.

Water does not decompose the borates of the alkali-metals, but it easily forms oxides from the borates of the heavy metals, which, on the other hand, are scarcely altered by concentrated solutions of neutral or acid sodium borate. Hence the reaction between alkaline borates and metallic salts, in very concentrated solutions, produces a pure metallic borate if the alkaline borate is in excess, and an oxide if the metallic salt is in excess, this oxide resulting from the decomposition of the metallic salt by water.

The action of *alkaline silicates* on metallic salts is similar to that of the borates. In the action of neutral sodium acetate on manganous sulphate, the production of oxide is due to the formation of sodium diacetate.

On the Reaction between Alkaline Carbonates and Earthy Oxalates, and between *Alkaline Oxalates and Earthy Carbonates*, see Watson Smith (p. 410 of this volume).

On the Decomposition of Solutions of Potash-alum at 100°, which takes place as a secondary result of the Dehydration of Crystallised Alum by Heat, see Naumann (p. 66).

On the Decomposition of Ammonium salts in Aqueous Solution alone, and when mixed with other salts, as the Chlorides or Nitrates of Potassium, Sodium, and Barium, see Dibbitts (p. 75).

Chemical Equilibrium between Hydrogen and Gaseous Iodine. The conditions of chemical equilibrium between these elements have been investigated by G. Lemoine (*Ann. Chim. Phys.* [6], xii. 145-253), with the view of determining the manner in which chemical combination in gaseous systems is affected by heat, by pressure, by the action of masses, by porous bodies, and by light. The combination of hydrogen and iodine-vapour is especially adapted for the study of these phenomena, as it exhibits ~~them~~ in their greatest degree of simplicity, the two elements being monatomic, and combining together in the gaseous state, and the combination not being attended with any very energetic thermal phenomena. The general result of the investigation is to show that the resolution of hydriodic acid into its elements takes place at the same temperature as the combination of hydrogen with gaseous iodine, but that, in a limited space, neither of these reactions is ever complete, and that they balance one another in such a manner that the same chemical equilibrium is ultimately attained whatever may be the point of departure; in other words, that the phenomenon is one of dissociation.

Influence of Heat and of Pressure.—The rapidity of the action varies with temperature and pressure between very wide limits, especially with differences of temperature. At 440° equilibrium is nearly attained in an hour; at 350° it is not complete for several days; and at 265° the time required for its attainment must be reckoned by months. The decomposition of hydriodic acid at this last temperature is perhaps the slowest that has been observed in mineral chemistry, and this result is doubtless to be attributed to the small intensity of the heat-effect produced by the union of hydrogen and gaseous iodine.

The acceleration of chemical action by heat is well known as a general fact. Etherification, for example, takes years to complete at ordinary temperatures, whereas it takes place very quickly at 200°; and the allotropic modification of phosphorus is produced more rapidly as the temperature is higher.

The rapidity of the combination is likewise affected by pressure, a state of equilibrium being much more quickly attained when the gases are under strong pressure, that is to say, when their molecules are brought within very short distances of each other; in rarefied gaseous systems, on the contrary, the establishment of equilibrium

is much slower, since the molecules of the two gases, being very far removed from one another, have much fewer chances of meeting so as to produce combination.

The magnitude of the limit of combination of hydrogen and iodine-vapour is considerably affected by temperature, but not much by pressure. The higher the temperature, the greater is the proportion of hydriodic acid decomposed. This result is in accordance with those obtained in most cases of dissociation, as in that of amylene hydrobromide (Wurtz, *Compt. rend.* lx. 729); of phosphorus pentachloride (Cahours, *ibid.* xxi. 625; lxiii. 144; Wanklyn & Robinson, *ibid.* lvi. 195, 322; H. Deville, *ibid.* lxii. 1157); and of the compound which Friedel obtained in endeavouring to combine hydrochloric acid with methyl oxide (*Bull. Soc. Chim.* [2], xix. 451).

The variations in the limit produced by pressure are very small, though at a temperature of 440° they are perceptible. Under strong pressure the combination of iodine and hydrogen is somewhat more complete than when the gases are very much diluted; and the same is found to be the case in the combination of hydrochloric acid and methyl oxide studied by Friedel. In the etherification of gaseous bodies also, the proportion of acid etherified is greater under high than under low pressures (Berthelot, *Ann. Ch. Phys.* [3], lxviii. 239).

Influence of Mass.—When one of the elements is in excess of its equivalent proportion, it is still found that a definite state of equilibrium is arrived at, and more rapidly than when the two elements are in equivalent proportions, and that the whole of the possible hydriodic acid is never formed, however great the excess of one of the elements. As the proportion of iodine present to the hydrogen present gradually increases, the quantity of hydriodic acid formed increases also gradually, without any sudden changes in value. The effects of pressure are very slight, but still in the same direction as before.

Action of Porous Bodies.—These seem to act only by bringing the molecules closer together, and therefore, as is the case with high pressures, they lessen the time of attaining a state of equilibrium, but do not sensibly alter the proportions in that state.

Action of Oxygen.—Oxygen decomposes hydriodic acid, either gaseous or in solution, at ordinary temperatures, though the action is very slow.

Action of Sunlight.—A solution of hydriodic acid is not affected by sunlight, nor does a mixture of iodine and hydrogen combine sensibly under its influence. On the other hand, gaseous hydriodic acid is decomposed by sunlight, and since there is no inverse tendency to recombine by the action of light, the decomposition is probably unlimited. In one case, by exposure of a bulb filled with the vapour to full daylight for a summer month, 80 per cent. of the acid was decomposed.

The great power of light to overthrow a molecular structure, which is destroyed but slowly and partially by heat, is very remarkable. The difference arises doubtless from the fact, that in the case of light the body is submitted exclusively to a decomposing action, whereas in the case of heat alone there are two opposing influences acting simultaneously, one tending to decompose, and the other to reproduce the combination, the former of these opposite forces being heat, and the latter chemical affinity, meaning by that term the aggregate of causes which tend to effect the recombination of dissimilar atoms.

Mutual Replacement of Halogen Elements. Bromine does not act upon the anhydrous chlorides of calcium, barium, and strontium, at temperatures below 200°, and the quantity of chlorine replaced by bromine depends chiefly on the temperature. From barium chloride, from 6 to 96 per cent. chlorine is expelled between 250° and a red heat. The time of action and the quantity of bromine present appear to exert no great influence. When bromine acts on a mixture of the three chlorides above mentioned, the quantity of chlorine replaced is greater the higher the atomic weight of the corresponding metal (A. Potilizin, *Dut. Chem. Ges. Ber.* vii. 733).

Mercuric chloride heated for six hours in a sealed tube to 250° with water and iodine is for the most part decomposed; *mercuric bromide* is not attacked by iodine either with or without water. On *auric* and *platinic chloride*, as well as on solutions of *palladium chloride*, iodine acts after some time even at ordinary temperatures. When *arsenious chloride* and *iodine*, both dry, are heated together in a tube to 100°, fine red crystals separate on cooling, probably consisting of a compound of arsenious chloride with iodine chloride. *Antimony pentachloride*, heated with iodine to 100° in a sealed tube, yields black crystals containing chlorine and iodine, together with antimony (F. Gramp, *ibid.* 1723).

The following table, constructed from the experiments by G. Gustavson (*Ann. Chim. Phys.* [5], ii. 200), gives the mean values in percentages of the double decomposition which takes place, when the several pairs of bodies mentioned are heated together in sealed tubes to 150°–200°. The numbers in brackets are not the results of direct experiment, but are calculated from the result of the inverse reaction:

Mixture.	Mean Value of Reaction.	Mixture.	Mean value of Reaction.
4BrCl ⁴ + 3CBr ⁴	10.12; (10.20)	TiBr ⁴ + CCl ⁴	(56.39)
4BBr ³ + 3CCl ⁴	89.97	4AsCl ³ + 3CBr ⁴	71.78
SiCl ⁴ + CBr ⁴	12.46	4AsBr ³ + 3CCl ⁴	28.91
SiBr ⁴ + CCl ⁴	(87.54)	SnCl ⁴ + CBr ⁴	97.52
TiCl ⁴ + CBr ⁴	43.61	Sn Br ⁴ + CCl ⁴	22.16

These numbers lead to the following conclusions: The higher the atomic weight of the element (B, Si, Ti, As, Sn) united with chlorine, the more will the chlorine be replaced by the bromine of the carbon tetrabromide; and the higher the atomic weight of the element united with bromine, the less will that bromine be replaced by the chlorine of carbon tetrachloride.

Relations of Affinity in the Imperfect Combustion of Gases and Gaseous Mixtures. Bunsen, from experiments on the amounts of hydrogen and carbon monoxide, which are burnt when mixtures of these gases are detonated with quantities of oxygen less than sufficient for their complete combustion, was led to conclude that the proportion by volume of the products (water-vapour and carbon dioxide) formed in this imperfect combustion, may always be expressed by small whole numbers, and that, consequently, while the proportion of hydrogen in the original mixture is increased continuously, the proportion of the products of combustion alters by definite increments or sudden leaps (see *CHEMICAL AFFINITY*, i. 860).

Similar experiments have since been made by E. v. Meyer (*J. pr. Chem.* x. 273; xiii. 121; *Chem. Soc. J.* 1876, ii. 40), who regards the results as decidedly confirmatory of those obtained by Bunsen. Horstmann, on the other hand (*Deut. Chem. Ges. Ber.* x. 1626), is of opinion that Bunsen's experiments were too few in number to establish the conclusion based upon them, and that the results of v. Meyer's experiments are not sufficiently definite to have any real bearing on the question. From his own experiments Horstmann infers that the variation in the proportion of water to carbon dioxide, formed under the circumstances above mentioned, is not intermittent but continuous.

1. Von Meyer's Experiments.

The following tables contain the results of a series of experiments on the imperfect combustion of mixtures of carbon monoxide and hydrogen with oxygen or nitrogen monoxide, and on the influence of nitrogen and of narrow tubes on the combustion of mixtures of CO and H. The 'coefficient of affinity' in the last column expresses the ratio between the affinities of equal volumes, and therefore also of equal numbers of molecules, of H and CO for O, or the proportion in which the affinity of 1 vol. CO for O is surpassed by that of an equal volume of hydrogen.

Number of experiment	100 vol. mixture contain H	100 vol. mixture contain CO	Oxygen employed for 100 vol. mixture	O. referred to quantity required for complete combustion = 1	Burnt H burnt CO	Coefficient of Affinity
1 {	a	.	31.95	0.6390	2 : 1	2.0
	b	50.0	17.75	0.3550	3 : 1	3.0
	c	1	19.75	0.3850	3 : 1	3.0
2 {	a	50.6	11.80	0.2360	3 : 1	2.93
	b		15.15	0.3030	3 : 1	2.93
			with N ² O			
	c	1.024	32.30	0.6460	2 : 1	1.953
	d		20.18	0.4036	3 : 1	2.93
			with N ² O			
3 {	a	57.75	30.90	0.6180	3 : 1	2.19
	b	1.367	22.76	0.4552	4 : 1	2.93
4 {	a	67.35	35.90	0.7180	4 : 1	1.94
	b	2.063	20.73	0.4146	6 : 1	2.91
5 {	a	67.70	34.05	0.6810	9 : 2	2.06
	b	2.096	14.35	0.2870	7 : 1	2.34
6 {		75.8	10.75	0.2150	10 : 1	3.195
		3.132				

Number of experiment	100 vol. mixture contain		Oxygen employed for 100 vol. mixture	O. referred to quantity required for complete combustion = 1	Burnt H : burnt CO	Coefficient of Affinity
	H	CO				
7	81.89 4.522	18.11 1	10.85	0.2170	14 : 1	3.096
8 {	82.26 4.64	17.74 1	10.34	0.2068	14 : 1	3.018
9 {	85.11 5.718	14.89 1	8.94	0.1788	19 : 1	3.325
with N ₂ O						
10 {	37.0 1	63.0 1.702	20.1	0.402	3 : 2	2.55
11 { a b c	26.8 1	73.2 2.702	24.6 13.85 12.25	0.492 0.277 0.245	3 : 1 1 : 1 1 : 1	2.05 2.75 2.75
12 { a b	25.45 1	74.55 2.93	35.85 8.55	0.717 0.171	1 : 2 4 : 5	1.47 2.35
13 { a b c	24.15 1	75.85 3.141	39.50 28.30 9.60	0.790 0.566 0.192	2 : 5 1 : 2 4 : 5	1.26 1.572 2.51

II. Experiments on the Influence of Nitrogen.

Number of experiment	100 vol. mixture contain		Oxygen employed for 100 mixture	Nitrogen employed for 100 (H + O)	Burnt H : burnt CO	Coefficient of Affinity (that of CO=1)
	H	CO				
14 { a b	52.05 1.086	47.95 1	28.0 28.0	— 134.0	5 : 2 5 : 1	2.302 1.8417
15 { a b	58.65 1.419	41.35 1	18.35 18.35	— 114.95	9 : 2 3 : 1	3.17 2.114
16 { a b	67.10 2.04	32.90 1	18.75 18.75	— 100.0	7 : 1 9 : 2	3.431 2.206
17 { a b	67.70 2.096	32.30 1	21.35 21.20	— 79.8	7 : 1 6 : 1	3.340 2.863

III. Experiments on the Influence of Narrow Tubes.

Number of experiment	100 vol. mixture contain		Oxygen employed for 100 mixture	Nitrogen employed for 100 (H + O)	Burnt H : burnt CO	Coefficient of Affinity
	H	CO				
18 { a b	64.0 1.777	36.6 1	16.06 —	21.0 12.5	6 : 1 13 : 2	3.428 3.714
19 { a and b c and d	56.57 1.303	43.43 1	19.73 —	26 and 21 5.5	10 : 3 4 : 1	2.558 3.070
20 { a b and c	44.65 1	55.35 1.24	16.27 —	20.0 5.5	9 : 4 9 : 4	2.79 2.79
21 { a and b c	39.48 1	60.52 1.553	18.95 —	20.0 9.0	8 : 5 2 : 1	2.452 3.066

In all cases the results of these experiments are in accordance with the law laid down by Bunsen (i. 860) that the burnt portions of a gaseous mixture are to one another in atomic, or rather in molecular proportion. The same law holds good when nitrous oxide is used instead of oxygen, as well as under circumstances which exert a modifying influence on the affinities of hydrogen and carbonic oxide, namely when the gaseous mixture is diluted with nitrogen, and when it is burned in narrow tubes. It must be observed, however, that besides the simpler ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4, &c. more complex ratios likewise occur, such as 5 : 2, 9 : 2, 5 : 4, 5 : 8, 10 : 3, &c.

In the combustion of *constant* mixtures of carbonic oxide and hydrogen with *varying* quantities of oxygen (in wide eudiometers) the coefficients of affinity attain their maximum when the quantity of oxygen used is as small as possible, so that the mixture approaches to the limit of inflammability. For gaseous mixtures in which the volume of hydrogen is equal to or greater than that of the carbonic oxide (H : CO varying between 1 : 1 and 5.718 to 1) the maximum values of the coefficients of affinity vary between 2.98 and 3.43, the mean of all the determinations being 3.14. In mixtures containing more carbonic oxide than hydrogen, the maximum values fall below 3; the extreme limits are 2.75 and 2.36; the mean of the experiments 10 to 13 is 2.54.

On account of the discontinuous alteration of the burning gases, it is impossible to obtain absolutely constant values of the coefficients of affinity: the relative constancy of these coefficients is therefore remarkable. Experiments 1 to 13 show that, with increase of hydrogen, the ratio of the affinities of H and CO remains the same, whereas with increase of carbonic oxide, a decided strengthening of the affinity of this gas for oxygen becomes perceptible. With increasing quantities of oxygen also, there is a distinct tendency to a diminution of the coefficients of affinity when the carbonic oxide is in excess, as appears from consideration of the experiments made with approximately equal quantities of oxygen. [See in the tables (2d and 10), (1c, 15a and 16a), (4a and 12a), (2b and 11c), (13b and 14a)]. With increased oxygen, the coefficients of affinity diminish by jerks, and approach to a minimum. The original proportion of H : CO seems never to be reached, since the hydrogen, in consequence of its greater affinity for oxygen, is completely burnt, even when some carbonic oxide still remains over.

The *admixture of Nitrogen*, an *indifferent gas* which takes no part in the combustion, influences this process in such a manner that the affinity of the hydrogen for oxygen is weakened, while that of the carbonic oxide is increased in a corresponding degree. This action is particularly strong when, in the combustion of the mixture *without* addition of nitrogen, the coefficient of affinity is nearest to its maximum. Thus the coefficient 3.431 (exp. 16a) is reduced to 2.206 (exp. 16b), whilst in experiments 15a and b a relatively larger quantity of nitrogen gives rise to a diminution of the coefficient from 2.302 to 1.8477. The influence of the nitrogen is similar in its effect to that of the carbonic oxide, but not comparable therewith, since the latter, by its partial combination with oxygen, takes part in the reaction.

When similarly composed mixtures of CO, H and O are detonated, *first in wide* and then in *narrow* tubes, the experiments for the most part exhibit different results in the two cases, the combustion in the narrow tube exhibiting an increase of affinity of the hydrogen and a diminution of that of the carbonic oxide. These experiments lead to the following important consequences: The changes of affinity produced, on the one hand, by addition of nitrogen, and on the other by combustion in narrow tubes, cannot be attributed—or at most in a very small degree only—to differences of temperature, since in both cases the temperatures are altered in the same sense, while the affinities are altered in the opposite sense. To explain the influence exerted upon affinity in narrow tubes, Meyer is of opinion that the principal factor to be taken into account is the *friction* of the gases. When this friction is increased, as when the combustion takes place in narrow tubes, the affinity of the hydrogen is for the most part increased, but never diminished.

2. Horstmann's Experiments.

Horstmann, as already observed (p. 430), takes a view of the results of the imperfect combustion of gaseous mixtures very different from that of v. Meyer, as detailed in the preceding pages. The main results of his investigations are summarised as follows:—

1. When carbon monoxide is detonated with increasing quantities of water-gas, as in Bunsen's experiments, the proportion of water-vapour to carbon dioxide in the products *increases continuously*. Whilst the proportion of hydrogen to carbon oxide increases from 0.25 : 1 to 2.33 : 1, or, in other words, whilst from 20 to 70 per

cent. of the combustible gases is burnt, the proportion of the products ($\text{H}^2\text{O} : \text{CO}^2$) varies from 0.8 : 1 to 4.5 : 1.

2. When a mixture of hydrogen and carbon oxide is detonated with increasing quantities of oxygen, as in v. Meyer's experiments, water-vapour and carbon dioxide are likewise formed in continuously increasing proportions.

The division of oxygen between the two combustible gases does not, therefore, take place in the manner supposed by Bunsen.

3. With moist gases less hydrogen and more carbon oxide are burnt than when the gases are dry. On the other hand, when carbon dioxide is present in the mixture before detonation, more hydrogen and less carbon oxide are burnt. [In the latter case some carbon dioxide would most probably be reduced by hydrogen in the detonation, and the proportion of carbon oxide burnt would, consequently, appear to be less.]

4. In experiments with mixtures of hydrogen and carbon oxide, the proportion of the products of combustion ($\text{H}^2\text{O} : \text{CO}^2$) varies in a peculiar manner. With increasing quantities of oxygen, this proportion increases at first, attains a maximum when 30.35 per cent. of the combustible gas is burnt, and then gradually decreases towards the limit that would be reached if the whole of the gases were burnt, i.e., towards the proportion of hydrogen and carbon oxide before detonation. Thus, for instance, in a mixture of hydrogen and carbon oxide containing 54.6 per cent. of hydrogen, the proportions of the products were successively 3.83, 4.09, 4.18, 3.96, 2.80, and 2.09 : 1, when the amounts of the gases burnt were respectively 21.7, 29.1, 34.9, 41.7, 53.9, and 66.2 per cent. of the whole.

5. The law according to which the oxygen is divided between the combustible gases may be expressed thus:—The proportion of the resulting water-vapour to the resulting carbon dioxide is equal to the proportion of the unburnt hydrogen to the unburnt carbon oxide, multiplied by a co-efficient of affinity which is independent of the proportion of the combustible gases, but varies with the relative quantities of oxygen added. This coefficient of affinity varies, according to Horstmann, between 4.0 and 6.4 when between 20 and 70 per cent. of the combustible gases is burnt, the maximum coefficient coinciding with the combustion of 30.40 per cent. of the gases. In other words, the proportion of water-vapour to carbon dioxide was found to be from 4.0 to 6.4 times as great as the proportion of hydrogen to carbon oxide in the residue unburnt. Hence, relatively more hydrogen than carbon oxide is burnt in all cases: the affinity of oxygen for hydrogen is greater than for carbon oxide.

6. The variability in the coefficient of affinity is due to the circumstance that the physical conditions of the reaction vary with the relative quantities of oxygen present. With equal quantities of oxygen the coefficient remains constant, not only when the proportion of hydrogen to carbon oxide is altered, but also when the unconsumed portion of the combustible gases is replaced, partially or entirely, by an indifferent gas of similar physical character, such as nitrogen, although the proportion of unburnt gases to the products of combustion varies in both cases.

Relations of Affinity in the slow oxidation of Hydrogen and Carbonic Oxide by means of Platinum (v. Meyer, *J. pr. Chem.* [2], xiii. 121; xiv. 124). The presence of carbonic oxide in mixtures of hydrogen and oxygen does not prevent but merely weakens the action of platinum. The greater the proportion of carbonic oxide present, the longer is the time required to bring the oxygen into a state of activity. The carbon monoxide is first converted into dioxide, and the union of hydrogen with oxygen in comparatively large quantity begins only when there is but a small quantity of carbon oxide remaining to be burnt.

The relative quantities of the two gases which are oxidised do not vary continuously but, as in the case of oxidation by explosion, discontinuously or by bounds, and in such a manner that the quantities of water and carbon dioxide formed in definite intervals of time, and therefore also the corresponding quantities of hydrogen and carbon monoxide, are to one another in simple molecular proportions.

The experiments on combustion by explosion show that when a mixture of hydrogen and carbonic oxide is exploded with an insufficient quantity of oxygen, the affinity of hydrogen for oxygen is on the average 3.14 greater than that of carbonic oxide; in the slow oxidation by the agency of platinum, on the contrary, the affinity of carbonic oxide for oxygen is found to exceed that of hydrogen in proportions ranging from 7.06 to 7.75; consequently the affinity of carbonic oxide for oxygen in the process of slow oxidation through the intervention of platinum, is from 22.2 to 24.3 times as great as the affinity of the same gas for oxygen when the oxidation takes place by explosion.

With a given proportion of hydrogen to carbonic oxide, the affinity of the latter for oxygen is diminished when the quantity of oxygen is increased. This is shown by the following results of experiment:—

H	CO	O	Coeff. of Affinity.
{ 100	26.05	38.0	3.90
{ 100	26.05	69.0	3.10
{ 100	47.6	49.65	6.30
{ 100	47.6	127.7	4.21

The proportion of carbonic oxide to hydrogen appears (within certain limits) to exert less influence on the relative affinities of the two gases for oxygen; thus in the following experiments in which the ratio H : O is nearly constant while that of H : CO varies, it will be seen that the coefficient of affinity varies but little:—

H	CO	O	Coeff. of Affinity.
100	42.54	22.14	7.06
100	52.00	27.20	7.70
100	64.50	23.27	7.75

On the other hand, considerable alterations in the relative affinities are produced by purely mechanical causes, as, for example, by the addition to the mixture of an indifferent gas, such as nitrogen, which in the case of slow combustion by means of platinum, as well as in that of rapid combustion by explosion, increases the affinity of carbonic oxide, and diminishes that of hydrogen for oxygen. The oxidation of the carbonic oxide is also favoured by the continual removal of the carbonic anhydride produced.

The affinity of hydrogen for oxygen in comparison with that of carbonic oxide is increased by elevation of temperature, and in this case also discontinuously, the law of oxidation in molecular proportions (of the products of combustion), holding good for high as well as for lower temperatures. This is seen in the following experimental results:—

H	CO	O	Temperature of Reaction.	Coefficient of Affinity (H=1).
{ 100	43.65	48.40	12°	7.65
{ 100	43.65	48.40	80°-90°	3.83
{ 100	64.50	23.27	4°-5°	7.75
{ 100	64.50	23.27	100°	3.10
{ 100	70.60	29.65	7°	9.90
{ 100	70.60	29.65	90°	7.80

To explain the oxidation of carbonic oxide before the hydrogen in these gaseous mixtures, v. Meyer supposes that carbonic oxide is more strongly attracted than hydrogen by the molecules of the platinum, an atmosphere of carbonic oxide being thus formed round these molecules, which to a certain extent prevents the hydrogen from coming in contact with them. Elevation of temperature may be supposed to loosen the attachment of the atmosphere of carbonic oxide to the platinum molecules, and at the same time to accelerate the movement of all the gaseous molecules in the mixture, thereby bringing the hydrogen and oxygen more freely into contact with the platinum, and increasing the relative proportion of the hydrogen oxidised. The presence of an indifferent gas like nitrogen, on the other hand, may be supposed to interfere with the access of the hydrogen molecules to the platinum, whereas it does not diminish the attraction of the platinum for the carbonic oxide: hence it will increase the relative affinity of the carbonic oxide.

The action of platinum in bringing about the combination of oxygen and hydrogen was attributed by De la Rive to the formation on the surface of the platinum of a thin film of platinumous or platinumic oxide, which was subsequently reduced by the hydrogen, this oxidation and reduction being continually repeated, so that the action becomes continuous, and a small quantity of platinum suffices to induce the combination of unlimited quantities of hydrogen and oxygen. If this were so, the oxides of platinum might be expected to act on a mixture of hydrogen and carbonic oxide in the same manner as platinum itself in presence of oxygen, that is to say, the proportions of the two gases oxidised would be the same in the one case as in the other. Such, however, is not the case: for when the oxidation is effected by the agency of platinumous or platinumic oxide, the coefficient of affinity of the carbonic oxide, referred to that of hydrogen as unity, is never much greater than 1.5 and sometimes less than 1, whereas when the oxidation is effected by free oxygen in presence of platinum, the coefficient of affinity of the carbonic oxide is sometimes equal to 8 or 9.

The following table exhibits the results of experiments in which the oxidation was effected by platinumous or platonic oxide:—

Original Proportion of the Gases.		Oxidising agent and Duration of the Action.	Coefficient of Affinity.
CO	H.		
100	69.6	PtO (15 min.)	0.819
100	68.6	PtO (50 min.)	0.686
100	153.4	PtO (1 min.)	0.614
100	153.4	PtO ² (240 min.)	1.534
100	76.0	PtO(OH) ² (120 min.)	1.140
100	111.5	PtO(OH) ² (18 hrs.)	1.190
100	111.5	PtO(OH) ² (12 hrs.)	0.970

On comparing these results with those above detailed, it is evident that the action of oxygen combined with platinum in the form of either platinumous or platonic oxide, on a mixture of hydrogen and carbonic oxide is totally different from that of free oxygen in presence of metallic platinum, and consequently that De la Rive's view of the action of platinum in the latter case, namely, that a film of oxide is first formed on the metal and then decomposed, must be regarded as untenable.

Imperfect Combustion of Hydrocarbons (v. Meyer, *J. pr. Chem.* [2], xiii. 121). When the incomplete combustion of the compounds CH_4 , C_2H_6 , C_2H_4 , C_2H_2 and $(\text{CH}_3)_2\text{O}$ yields only gaseous products, there is a tendency to the establishment of a molecular proportion between these products, expressible in whole numbers. If the quantities of oxygen are regulated so as to be at least sufficient to convert the whole of the carbon of the compound into monoxide, but *not* sufficient to oxidise the hydrogen, then it is possible to distinguish three portions, α , β , γ , of the gas in question, which stand to one another in more or less simple numerical relations. α is the portion which is completely burnt to CO_2 and H_2O ; β that which is burnt to CO and H_2O ; γ the residue in which the oxidation stops short at the formation of CO, the hydrogen not being attacked. Whether the combustion process takes place by successive stages, possibly in such a manner that the hydrocarbon is first oxidised to CO, with separation of hydrogen, and that this mixture is then partially oxidised, cannot be determined. But the experiments show that the carbon combined with the hydrogen before the explosion exhibits a strong tendency to lay hold of the oxygen to form CO, and this tendency is further shown by the following observations. This powerful affinity of carbon for oxygen makes itself felt indeed, even under the most unfavourable conditions, with a large excess of hydrogen and small quantities of oxygen. As soon as the first stage of oxidation is reached, the partially saturated affinity of the carbon in the carbonic oxide gives place to that of the hydrogen. An increase of oxygen exerts its influence in such a manner that $\alpha + \beta$ increases while γ proportionately diminishes; γ disappears first, β on the occurrence of complete combustion.

When hydrocarbons mixed with hydrogen are exploded with insufficient quantities of oxygen, molecular regularities are likewise exhibited in the proportions of the products of combustion. The question as to how much free hydrogen has taken part in the combustion must, however, remain undecided. The influence of this free hydrogen is shown in the decrease of α , and the considerable increase of β .

The presence of nitrogen appears to alter the proportion $\alpha : \beta : \gamma$.

On the Inflammability of Hydrocarbons, and the processes which take place in the most imperfect Combustions.—The following table shows the composition of inflammable and non-inflammable mixtures of hydrocarbons and oxygen, also of certain hydrocarbons with detonating gas.

Inflammability of Hydrocarbons.

Volume of combustible gas.	Oxygen employed	Quantity of O. employed, referred to that required for complete combustion, taken as =1	
1 { 1 vol. CH_4^*	0.825	0.4125	not inflammable
" "	0.876	0.4380	inflammable
2 { 1 vol. C^2H^6	0.968	0.2766	not inflammable
" "	1.007	0.2877	inflammable
3 { $\frac{1}{2}$ vol. C^2H^6 + $\frac{1}{2}$ vol. H_2	0.722	0.3610	not inflammable
" "	0.796	0.3980	inflammable
4 { 1 vol. $(\text{CH}^3)_2\text{O}$	1.056	0.3017	not inflammable
" "	1.355	0.3870	inflammable
5 { 1 vol. C^2H^4	0.533	0.1777	not inflammable
" "	0.637	0.2123	inflammable
6 { 1 vol. C^2H^2	0.184	0.0736	not inflammable
" "	0.2286	0.0914	inflammable

Mixtures of Detonating Gas with C^2H^6 or CH_4 .

Volume of combustible gas	Oxygen employed	Quantity of O. employed, referred to that required for complete combustion, taken as =1	
7 { 1 vol. C^2H^6 + 3.926 vol. H_2	1.963	0.3596	not inflammable
1 vol. C^2H^6 + 3.992 vol. H_2	1.996	0.3632	inflammable
8 { 1 vol. C^2H^4 + 2.448 vol. H_2	1.224	0.290	not inflammable
1 vol. C^2H^4 + 2.794 vol. H_2	1.397	0.318	inflammable

The most important results of these experiments may be summarised as follows. In the detonation of ethylene and acetylene with quantities of oxygen not sufficient to convert the whole of the carbon into carbonic oxide, the whole of the oxygen is consumed in the formation of that compound. If the combustion of ethylene under these circumstances is attended with separation of carbon, a quantity of the nascent carbonic oxide, increasing as the oxygen decreases, unites with an equal volume of ethylene to form acrolein according to the equation $\text{CO} + \text{C}^2\text{H}^4 = \text{C}^3\text{H}^4\text{O}$. The carbonic oxide, formed under similar conditions in the combustion of acetylene, does not possess the power of uniting in a similar manner with that hydrocarbon, but remains unaltered in the gas. In the cases of ethane, methane, and methyl oxide, it cannot be decidedly proved that the whole of the oxygen is employed in the oxidation of the carbon, since the higher limits of inflammability of these mixtures allow the combustion to go further.

The limits of inflammability of mixtures of hydrocarbons with oxygen depend upon the heat-phenomena which take place in the resolution of the hydrocarbons into carbon and hydrogen, and in such a manner that the limit is highest for that hydrocarbon (viz. methane), which, in separating into its components, *absorbs* the greatest quantity of heat, and lowest for that one (acetylene), the decomposition of which is attended with the greatest *evolution* of heat. The hydrocarbons, whose limits of inflammability lie between those determined for methane and acetylene must, therefore, when resolved into their constituents, evolve or absorb quantities of heat which, according to their inflammability, lie between the values determined for these two hydrocarbons. The behaviour of ethylene is in accordance with this law.

CINERY-LAUREL OIL. The essential oil of the common-laurel (*Cerasus Laurocerasus*) consists of benzoic aldehyde, hydrocyanic acid (less than 2 per cent.), a volatile oil, possibly benzyl alcohol, $\text{C}^7\text{H}^8\text{O}$, convertible by oxidation into benzoic acid, and minute quantities of an odorous resin (W. A. Tilden, *Pharm. J. Trans.* [3], v. 761).

* To render the values of the second column for CH_4 , as well as for mixtures of equal volumes of C^2H^6 and H_2 comparable with the rest, it is necessary to start from 2 vols of these gases: e.g. 2 vols. CH_4 require 1.752 vol. O to render the gas inflammable, &c.

CHESSYLITE. *Tricuprio Orthocarbonate*, $\text{Cu}^*\text{H}(\text{CO}^*)^2$ —(i. 738).—On pseudo-morphs of this mineral after Cuprite, see Geinitz, (*Jahrbuch f. Min.* 1877, p. 449; *Chem. Soc. J.* 1877, i. 697).

CHESTNUT. *Castanea vesca*.—Observations on the influence of the chemical composition of the soil on the growth of this tree have been made by Fliche a. Grandeau (*Ann. Chim. Phys.*, [5], ii. 354); Chatin (*Bull. Soc. Botan.* 1870, 194) has shown that the chestnut naturally disappears from soils containing more than 3 per cent. of lime. In accordance with this, Fliche a. Grandeau find that on a soil of the wood of Champêtre containing about 55 per cent. calcium carbonate, chestnuts will not grow; that on a calcareous soil of the same locality, containing 3.25 per cent. lime in the surface soil, and 24.04 per cent. in the subsoil, the growth is very poor and sickly, whereas on a silicious soil containing only 0.35 per cent. lime in the surface soil and 2.20 per cent. in the subsoil, it is vigorous. (For the analyses of these soils, see the article *Pinus* in this volume).

Analyses of the ash of the leaves and of the stem and branches from trees grown on the silicious and on the calcareous soil gave the following percentage results.

The well-grown specimens from the silicious soil were taken from a plantation about twelve years old, and the badly grown specimens from the calcareous soil from one twenty-three years of age.

	Leaves		Wood	
	From silicious soil	From calcareous soil	From silicious soil	From calcareous soil
P ₂ O ₅	12.32	12.50	4.53	4.27
SiO ₂	6.79	1.46	3.08	1.36
CaO	46.37	74.55	73.26	87.30
Fe ₂ O ₃	1.07	.83	2.04	1.27
MgO	6.63	3.70	3.99	2.07
K ₂ O	21.67	5.76	11.65	2.69
Na ₂ O	3.86	.66	—	.28
SO ₃	2.97	—	1.43	.64
Cl30	.52	—	.08
Percentage of ash	99.98	99.98	99.98	99.96
	4.80	7.80	4.74	6.71

The percentage of ash both in the leaves and in the stems and branches is greater in those plants grown on the lime soil, and in these there is a marked increase in the percentage of lime, and decrease in that of the potash and also of the silica. The percentage of iron is also deficient in those grown on the lime soil. Sodium and chlorine, which are present in the leaves, are nearly or quite absent from the wood.

The leaves from the trees on the lime soil were much smaller, and a microscopical examination showed that they contained far less starch and chlorophyll than those from the trees of vigorous growth.

Malaguti and Durocher (*Ann. Chim. Phys.* [3], liv. 257) found that several plants assimilated much more lime and much less potash when grown on a calcareous soil, and more recently Röthe (*Bot. Zeit.* 1872, 240) has observed the same facts with *Herniaria glabra*.

CHICORY. On the Detection and Estimation of Chicory in Coffee, see *COFFEE*.

CHILDRENVITE. This mineral from Tavistock (sp. gr. 3.22) has been analysed by Church, who assigns to it the formula $7\text{RO.2Al}_2\text{O}_3.3\text{P}_2\text{O}_5 + 12\text{H}_2\text{O}$ (in which R = Fe + Mn).

	FeO.	MnO.	MgO.	Al ₂ O ₃ .	P ₂ O ₅ .	H ₂ O.	O.
Analysis	26.63	7.74	1.03	15.85	30.65	17.10	0.29 = 99.29
Calculation	26.67	10.52	—	15.26	31.55	16.00	— = 100

The 0.29 per cent. oxygen corresponds with the quantity of iron present as Fe_2O_3 (*Chem. Soc. J.* [2], xi. 103).

CHINOLINE, $\text{C}^*\text{H}^*\text{N}$. This base is oxidised by potassium permanganate to leucolinic acid, $\text{C}^*\text{H}^*\text{NO}_2$ (q. v.), and this acid heated with soda-lime yields a distillate containing aniline:



(Dewar, *Proc. Roy. Soc.* xxvi. 65).

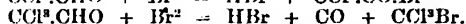
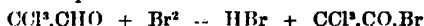
On the Physiological Action of the Chinoline and Pyridine bases, see McKendrick a. Dewar, *Pharm. V. Trans.* [3], v, 868; *Chem. Soc. J.* 1876, 1276).

CHLORACETAMIDE. See ACETAMIDE (p. 2).

CHLORACETONITRIL. See ACETONITRIL (p. 33).

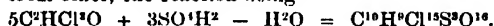
CHLORACETYL-UREA. See CARBAMIDES (p. 393).

CHLORAL, CCl_3CHO . *Reactions.* 1. With *Bromine*.—When bromine and chloral, in equal numbers of molecules, are heated together to 140° in sealed tubes opened from time to time to allow gas to escape, till the bromine has nearly disappeared and only a small quantity of gas is given off, the products obtained are bromotrichloromethane, trichloroacetyl bromide, hydrogen bromide, and carbon monoxide, formed according to the equations—



The products are difficult to separate by distillation. On adding water, the trichlorobromomethane separates out, and the trichloroacetyl bromide is converted into trichloroacetic acid (Oglialoro, *Deut. Chem. Ges. Ber.* vii. 1461).

2. With *Sulphuric acid*.—The compound, $\text{C}^6\text{H}^5\text{Cl}^{12}\text{S}^3\text{O}^{12}$, formed by the action of sulphuric anhydride on chloral (2nd Suppl. 308) may likewise be obtained by washing the product of the action of sulphuric acid on chloral with cold water, and crystallising the residue from ether, the reaction being—



This compound may, with care, be crystallised from warm alcohol. It melts at 70° , undergoing decomposition at the same time. At 100° chloral distils over, leaving a residuo of sulphuric acid and chloralide. It decomposes, by keeping, into sulphuric acid and insoluble chloral; with acetyl chloride it forms a compound, $\text{C}^6\text{H}^{12}\text{Cl}^{12}\text{S}^3\text{O}^{12}$, which crystallises in small needles, melting at 92° .

With *fuming sulphuric acid*, chloral yields the compound, $\text{C}^6\text{H}^5\text{Cl}^{12}\text{S}^2\text{O}^{12}$ (Grabowski, *Deut. Chem. Ges. Ber.* vi. 1070).

3. With *Nitrous Anhydride*.—When this gas is passed into anhydrous chloral, a deep green solution is formed, which does not change on standing. At 100° , however, in sealed tubes, a reaction takes place, yielding trichloroacetic acid and a small quantity of chloropierin, together with a very large quantity of gas (Wallach, *Liebigs Annalen*, clxxiii. 274).

4. With *Hydrogen Sulphide*.—This gas passed into anhydrous chloral at ordinary temperatures forms chloral sulphhydrate $(\text{CCl}_3\text{—CHOH})_2\text{S}$, (p. 441).

5. Chloral heated with *phosphorus pentasulphide* in sealed tubes to $160^\circ\text{--}170^\circ$, yields—together with hydrochloric acid and a brown amorphous solid—a liquid, which when decanted, distils for the most part between 84° and 93° , the temperature, however, rising towards the end to 140° , when a yellowish oil passes over, which is decomposed by water, with separation of sulphur, and probably consists of sulphur chloride. The portion boiling at 83° , when washed with water and distilled in a current of steam, yields an oily distillate, which, after drying with calcium chloride, has a very pleasant odour, boils at 88° , and agrees in other characters, and in composition with chloroacetylene dichloride or trichloroethylene, $\text{C}^6\text{H}^2\text{Cl}^3$ (2nd Suppl. 20). (Paternò a. Oglialoro, *Gazzetta chimica italiana*, iii. 538).

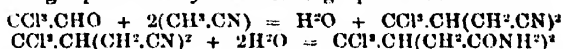
6. With *Acetyl chloride*.—Anhydrous chloral unites directly with acetyl chloride, forming the compound $\text{C}^6\text{H}^5\text{Cl}^3\text{O}^2 = \text{Cl}^3\text{C—CHCl—O—C}^6\text{H}^5\text{O}$, which is also produced, with rapid evolution of hydrochloric acid, when 1 mol. chloral hydrate is treated with rather more than 2 mol. acetyl chloride. The reaction is completed by heating the mixture on the water-bath, and on pouring the product into water, the compound $\text{C}^6\text{H}^5\text{Cl}^3\text{O}^2$ separates as a heavy oil, which, when purified in the usual way, boils at 185° (uncorr.), and has a density of 1.4761 at 17° (V. Meyer, *Deut. Chem. Ges. Ber.* iii. 445). According to Curie a. Millet (*Compt. rend.* lxxxiii. 745) it boils at $186^\circ\text{--}188^\circ$, is not sensibly attacked by water at 200° , but acts violently on pulverised potassium hydrate, with formation of chloroform, potassium chloride, and potassium acetate. Distilled over sulphuric acid, it yields chloral; over fused sodium acetate, it yields chloral and sodium chloride. Treated with zinc and acetic acid, it exchanges 2 at. chlorine for 2 at. hydrogen, and is converted into the compound $\text{C}^6\text{H}^5\text{Cl}^2\text{O}^2$, metameric with ethylic dichloroacetate and dichloroethylic acetate, which boils without decomposition at $146^\circ\text{--}148^\circ$, and reacts like a compound of monochloraldehyde and acetyl chloride.

7. With *Hydrocyanic acid*.—When chloral is cohobated for some days in the water-bath with hydrocyanic acid and hydrochloric acid, a clear yellow liquid is

obtained, which, when evaporated at 100° gives off hydrocyanic acid, and finally leaves a mass of sal-ammoniac crystals mixed with a yellow oil. On treating this mass, after cooling, with ether, the oil is dissolved, and separates, on evaporating the ether, as a thin syrup which solidifies on standing. The product thus obtained is a mixture of trichlorolactic acid and chloral cyanohydride, $\text{CCl}^3\text{CH}(\text{OH})\text{CN}$.

This addition-product is not formed by the action of anhydrous hydrocyanic acid on chloral at a moderate heat (28°), but is easily prepared by digesting a mixture of chloral with a concentrated aqueous solution of hydrocyanic acid for several hours, and evaporating the product on the water-bath. The mobile oil which is left solidifies on cooling to a mass of colourless prisms, which may be readily purified by recrystallisation from water. It is very easily soluble in alcohol and ether, and volatilises slightly with the vapour of water, being at the same time decomposed into chloral and hydrocyanic acid. Alkaline solutions cause it to split up into chloroform, formic acid, and hydrocyanic acid. It melts at 60°–61°. When digested at 100° for several days with strong hydrochloric acid, it is converted into trichlorolactic acid, $\text{C}^3\text{H}^2\text{Cl}^3\text{O}^2 = \text{CCl}^3\text{—CHOH—COOH}$, melting at 105°–110° (Pinner a. Bischoff, *Liebigs Annalen*, clxxix, 174).

9. With *Methyl cyanide* or *Acetonitril*.—This reaction yields a compound which may be regarded as the amide of a chlorinated bibasic acid, $\text{CCl}^3\text{—}(\text{CH}(\text{CH}^2\text{CONH}^2))^2$, its formation being represented by the following equations:

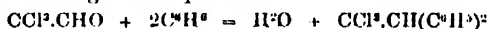


(Hübner a. Schreiber, *Zeitschr. f. Chem.* 1871, 712; Hübner, *Deut. Chem. Ges. Ber.* vi, 109).

10. With *Cyanamide*.—See CYANAMIDE.

11. With *Allyl alcohol*.—See p. 60.

12. With *Benzene* and its derivatives. —When 1 mol. chloral and 2 mol. benzene are mixed with about double the volume of strong sulphuric acid, diphenyl-trichloroethane is formed, according to the equation:



(Goldschmidt, *Deut. Chem. Ges. Ber.* vi, 985).

In like manner with *monobromo-* and *monochlorobenzene*, chloral forms the compounds $\text{CCl}^3\text{CH}(\text{C}^6\text{H}^4\text{Br})^2$ and $\text{CCl}^3\text{CH}(\text{C}^6\text{H}^4\text{Cl})^2$, both of which are crystalline (Zeidler, *ibid.* vii, 1180); and with *toluene*, dimethylphenyltrichloroethane, $\text{CCl}^3\text{CH}(\text{C}^6\text{H}^4\text{CH}^3)^2$, which separates from solution in ether-alcohol in fine crystals melting at 89° (Fischer, *ibid.* vii, 1191).

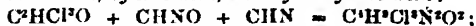
13. With *Thymol*.—A mixture of chloral and thymol treated with sulphuric acid and glacial acetic acid, yields dithymoxyl-trichloroethane, $\text{CCl}^3\text{CH}(\text{C}^6\text{H}^4\text{O})^2$ (Jäger, *Deut. Chem. Ges. Ber.* vii, 1157). See DITHYMOXYL-COMPOUNDS.

14. With *Amines and Amides*.—See 2nd Suppl. 311. With *aniline* and its homologues the products are trichloroethyleno-diphenylamine, $\text{CCl}^3\text{CH}(\text{NH}\cdot\text{C}^6\text{H}^5)^2$, and the corresponding tolyl and xylyl bases. The tolyl base, discovered by Wallach, has been further examined by Amato. See PHENYLAMINES.

15. With *Oxyacids*.—See CHLORALIDE.

On the compounds of chloral with *Albuminoids*, and on its physiological action, see Personne (*Compt. rend.* lxxviii, 126) and Byasson (*ibid.* 649); also *Chem. Soc. J.* 1874, 355, 591. On the physiological action of chloral, see also Tomaszewicz (*Pföüger's Archiv. f. Physiologie* ix, 35; *Chem. Soc. J.* 1874, 814).

Chloral Cyanido-cyanate, $\text{C}^3\text{H}^2\text{Cl}^3\text{N}^2\text{O}^2$. This compound is formed on mixing the dilute solutions of chloral and potassium cyanide containing cyanate. A gradual reaction then takes place at ordinary temperatures, hydrocyanic acid is evolved, the mixture becomes warm, and after some hours deposits prismatic crystals, which are larger the more dilute the solutions are employed. The compound thus formed contains the elements of chloral, cyanic acid, and hydrocyanic acid:



not a trace of it is produced by treating chloral hydrate either with pure cyanide or pure cyanate.

Chloral cyanido-cyanate melts at 80°, and when heated in a closed tube sublimes partially at 100° in long needles, and carbonises at 120°. It is soluble in ether and in alcohol, and separates therefrom in crystals. It dissolves sparingly in cold, easily in hot water, and is completely decomposed thereby, with formation of hydrocyanic and formic acids. On heating it with water in sealed tubes, hydrocyanic acid is eliminated, and the liquid yields ammonium chloride on evaporation. When distilled with water, it is resolved into hydrocyanic and hydrochloric acids, carbon dioxide

and formic acid. It dissolves in dilute acids and crystallises therefrom unaltered, but when heated with dilute hydrochloric acid, it yields ammonium chloride.

On the reaction of Chloral Cyano-cyanate with *Aniline*, see CHLORAL-ANILIDE (p. 443).

Chloral Hydrate, $C^2H^3Cl^3O^2 = C^2HCl^3O.H^2O = CCl^3.CH(OH)^2$. This compound is now manufactured on a very large scale, some German makers supplying as much as 250 kilograms daily. Chlorine is passed into alcohol of at least 96 per cent. For 120–150 lbs. of alcohol the current of chlorine must be maintained for 12–14 days, in which time the temperature rises to 60° – 75° , and the liquid acquires the density of 41° B. The crude product thus obtained is purified by heating it with an equal weight of strong sulphuric acid in copper vessels lined with lead. Considerable quantities of hydrochloric acid escape at first, and afterwards chloral distils at 95° – 100° . This distillate is redistilled, collected in glass flasks, and mixed with water; and the hydrate then formed is either poured into large porcelain basins, in which it solidifies in cakes in half an hour; or it is poured into vessels one-third full of chloroform, to crystallise (G. Detsenyl, *Chem. Centr.* 1873, 767).

Vapour-density.—A. Naumann (*Deut. Chem. Ges. Ber.* ix. 822) has made experiments on the density of the gases obtained by heating chloral hydrate, from which he infers that this substance cannot exist in the state of vapour, but undergoes dissociation into C^2HCl^3O and H^2O when volatilised even at ordinary temperatures. The values obtained are shown in the following table:

Density of the Gases evolved from Chloral Hydrate.

Quantity of Substance	Temperature	Pressure mm.	Volume cub. cent.	Density	
				Calculated for C^2HCl^3O H^2O	$C^2H^3Cl^3O^2$
0.2205	100°	450.5	136.7	2.81	
0.0520	78.5	162	85.8	2.83	5.72

According to these numbers, the resolution of 1 mol. chloral hydrate into two separate gas-molecules is complete even at 78° ; and further, when a quantity of chloral hydrate more than sufficient to fill the space above it with vapour, was heated for some time to about 35° , and then cooled, the tension of the vapour was found to be always below 6 mm.: hence it may be inferred that chloral hydrate cannot pass into the state of vapour without decomposition even at ordinary temperatures. At higher temperatures, the dissociation-tension of the chloral hydrate did not attain a constant value even after a considerable time. At 35° it rose gradually in an hour from 12 to 17 mm.; at 46° in $\frac{1}{2}$ hours from 18 to 47.5 mm.; at 78° in forty minutes, from 261 to 296 mm. The highest tension, according to the last observation made at each temperature, must not be regarded as a true maximum, but only as a lower limit, which would be exceeded if the heating were continued longer.

Troost, on the other hand (*Compt. rend.* lxxxiv. 708; lxxxv. 32, 400), having been unable to detect the presence of aqueous vapour in the gases evolved from chloral hydrate, infers that this compound does not undergo dissociation when vaporised, but exists in the state of vapour as an entire molecule, $C^2H^3Cl^3O^2$, the vapour-density of which is therefore anomalous, indicating a condensation to 4 vols. instead of the usual 2 vol. condensation. The mode of experimenting employed by Troost depends upon the following considerations. If the vapour be really in a state of dissociation, it will behave like a mixture of equal volumes of aqueous vapour and dry gaseous chloral. Denoting, therefore, the total vapour-tension by F , each of these gases will have a tension equal to $\frac{F}{2}$, and on introducing into the mixture a hydrated salt,

whose tension of dissociation is known to be less than $\frac{F}{2}$, the total tension of the vapour in the apparatus will remain unchanged, that is, equal to F ; for the salt will be in presence of a greater proportion of aqueous vapour than it could itself give off at the same temperature. If, on the other hand, the hydrate of chloral exists undecomposed in the vapour, the salt will be dissociated as in dry gas, and the total tension will consequently be increased, and will tend to become $F + f$.

The salt employed in the experiments was neutral potassium oxalate, which has

at 78° a dissociation-tension of 53 mm. The elastic force of the vapour of the chloral hydrate at 78° was 117.5 mm.; but on addition of the oxalate, the tension in the vessel gradually increased, till 164.5 was reached. The hydrated salt had therefore become dissociated in the vapour nearly as in a dry gas. The same result was obtained by vaporising chloral hydrate in a space already containing vapour of water omitted by a hydrated salt. Hence Troost infers that, contrary to the received opinion, chloral hydrate can exist in the gaseous state at 78°, and that its molecule exhibits a 4 vol. condensation.

According to Wurtz, on the contrary, crystallised potassium oxalate does not give off its water in the vapour of chloral hydrate, although in that of chloral ethylate, $C^2HCl^3O.(C^2H^3O)$, it parts with its water as easily as in air.

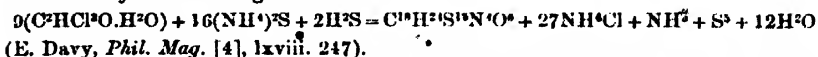
The question as to the dissociation of chloral hydrate cannot, therefore, at present be regarded as completely decided; but the agreement of Wurtz's result with that of Naumann, obtained by a totally different method, certainly gives support to the conclusion that this compound in passing into the state of vapour is really resolved into chloral and water.

Reactions.—1. When chloral hydrate is heated with five times its weight of syrupy glycerin, a regular action begins at 110° and goes on up to 230°, at which temperature the operation must be stopped to avoid complicating the results. The distillate consists of chloroform, formic acid, and undecomposed chloral hydrate, besides hydrochloric acid and allyl chloride, which are secondary products (Byasson, *Compt. rend.* lxxv. 1628).

2. Chloral hydrate is decomposed by an alkaline solution of *potassium permanganate*,—manganese sesquioxide being precipitated, and potassium carbonate, formate, and chloride remaining in solution, while carbon oxide is evolved. This fact leads to a theory of the action of chloral in the animal organism. When it is introduced into the circulation, the alkalinity of the blood and the oxidising agencies present are favourable to the production of carbon oxide, which, according to the experiments of Cl. Bernard, can combine with the blood-globules, displacing the oxygen. These globules thus become unfit for any physiological function, and can only be revived by the displacement of the carbon oxide. Bernard has also observed a decrease of temperature in cases of partial poisoning by carbon oxide, and this coincides with the results which follow the administration of chloral. The slow decomposition of chloral by an oxidising agent also explains the continuity of its action as a hypnotic, which would not be the case if it were transformed into chloroform (Tanret, *J. Pharm. Chim.* [4], xx. 355).

3. When *ammonium sulphide* is added to an aqueous solution of chloral hydrate, the mixture rapidly turns yellow, and, after passing through several shades of colour, finally becomes dark brown. From this liquid, dilute sulphuric acid throws down a bulky brown precipitate which may be purified by washing and exhaustion with carbon sulphide, to remove free sulphur, and dried at 100° till its weight becomes constant. It then presents the appearance of an amorphous light brown, earthy powder, slightly soluble in water, alcohol, and carbon sulphide, nearly insoluble in chloroform and benzene, but readily soluble in solutions of caustic alkali and alkaline sulphides, from which it is reprecipitated on the addition of an acid. When ignited on platinum foil, it evolves a peculiar odour, and, taking fire, produces a large carbonaceous residue which slowly burns away.

Its analysis leads to the formula $C^3H^4S^3N^3O^3$, from which it may be supposed to be formed by the following reaction:—



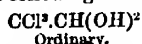
4. The action of *hydrogen sulphide* on chloral hydrate gives rise to chloral sulphhydrate (p. 442).

5. With a mixture of *Potassium Cyanide* and *Cyanate*, chloral hydrate, as already observed, yields chloral cyanido-cyanate, $C^3H^3Cl^3N^3O^3$ (p. 430); but on mixing it in concentrated aqueous solution, with pure *potassium cyanate*, carbon dioxide is speedily evolved in large quantity, and crystals separate, difficultly soluble in water, ether, and alcohol. They are decomposed by boiling alkalis, with evolution of ammonia, and carbonise above 200° without melting. On analysis they give numbers agreeing with the formula $C^3H^3Cl^3N^3O^3$, differing by the elements of hydrochloric acid from the body which is obtained by the simultaneous action of potassium cyanate and cyanide on chloral hydrate. Other substances not yet fully examined are also formed in the reaction. If too strong solutions are used, a brown coloration is produced, and the product is partially resinised.

Thiocyanate and *ferrocyanide* of potassium likewise act energetically on chloral hydrate (Wallach, *Dent. Chem. Ges. Ber.* viii. 1327).

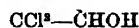
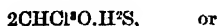
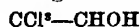
442 CHLORAL SULPHYDRATE—CHLORAL-AMMONIA.

Isomeric Chloral Hydrate.—Chloral mixed with *glacial acetic acid* is converted, according to the conditions of the experiment, either into ordinary chloral hydrate or a compound isomeric therewith. By quick evaporation of the mixture, the isomeric compound is obtained in fine crystals melting at 80° ; by slow evaporation, the same mixture yields ordinary chloral hydrate melting at 57° , or mixtures of the two (m. p. 60° – 80°). The constitution of the two hydrates may perhaps be represented by the following formulæ:



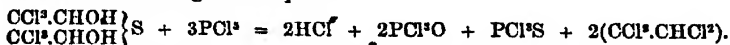
but it is also possible that they may be polymeric (V. Meyer, *Deut. Chem. Ges. Ber.* vi. 449).

Chloral Sulphhydrate. Byasson, by passing gaseous hydrogen sulphide into anhydrous chloral, at ordinary temperatures, obtained a crystalline compound to which he assigned the composition of chloral sulphhydrate, $\text{CHCl}^3\cdot\text{O}\cdot\text{H}^2\text{S}$ or $\text{CCl}^3\text{—CH}\left\{\begin{smallmatrix}\text{OH} \\ \text{SH}\end{smallmatrix}\right.$ (2nd Suppl. 312), and Hagemann (*ibid.*) by passing the same gas into a solution of anhydrous chloral in ether, obtained a solid body having the composition—



The product of this reaction has been further examined by Paternò & Ogliaro (*Gazz. chim. ital.* 1873, 533), who have not been able to obtain Byasson's product, even when following his directions exactly, but have always obtained the compound described by Hagemann: and the same result has been obtained by G. Wyss (*Deut. Chem. Ges. Ber.* vii. 211). This compound is insoluble in water, and decomposes gradually in contact with that liquid; in absolute alcohol and in ether it dissolves without alteration; it is very slightly soluble in cold chloroform, more easily when the liquid is warmed, forming a solution which has a great tendency to remain super-saturated (P. and O.) According to Wyss it dissolves in all proportions in alcohol and ether, and freely in benzene, chloroform and carbon sulphide, separating from these solutions in rhombohedral crystals, melting with decomposition at 127° – 128° . When recently crystallised and dried over sulphuric acid, it is nearly scentless, but on exposure to the air it acquires a disagreeable odour, like that of sulphuretted ethers. It melts at 128° when pure, but the melting point is apt to be lowered a few degrees, in consequence of the great alterability of the compound. On distillation it boils at 100° – 115° , the greater part solidifying during distillation, and consisting of the unaltered products; but the first portions of the distillate are liquid and contain chloral. This circumstance, together with the rather low melting point, indicate that the compound is decomposed by heat (P. and O.)

Chloral sulphhydrate is decomposed by strong sulphuric acid and by phosphorus oxychloride, with evolution of hydrogen sulphide, but no definite products of the reaction have been obtained. Heated with phosphorus pentachloride it yields pentachlorethane, according to the equation—



With phosphorus trichloride it appears also to yield pentachlorethane, and with potassium cyanide it forms thiocyanate.

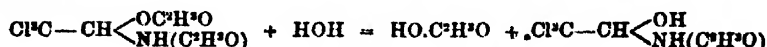
Heated in a reflux apparatus with acetyl chloride, it yields the diacetyl-derivative, $[\text{Cl}^3\text{—CH}(\text{OC}^2\text{H}^3\text{O})]^2$, which, after separation by water and washing, forms an unctuous mass, and may be obtained by recrystallisation from alcohol in fine prismatic crystals. It melts at 78° , dissolves easily in benzene and chloroform, is nearly insoluble in water, and is not attacked at ordinary temperatures by acids or alkalis (Wyss).

When a dilute aqueous solution of chloral hydrate is treated with hydrogen sulphide, an oily fetid liquid is formed, which appears to be a mixture (Wyss).

CHLORAL-AMMONIA, $\text{CHCl}^3\cdot\text{O}\cdot\text{NH}^3 = \text{Cl}^3\text{C} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CH} \begin{smallmatrix} \text{OH} \\ \text{NH}^3 \end{smallmatrix}$. To prepare this compound, anhydrous chloral is dissolved in $1\frac{1}{2}$ times its weight of dry chloroform; the solution is cooled in ice; and a rapid current of ammonia is passed into it, till the whole suddenly solidifies. The mass is then thrown upon a vacuum filter, to free it from chloroform, washed with ether, and spread on paper to dry. Chloral-ammonia thus obtained is nearly pure. It is a dazzling white body, nearly insoluble in water, sparingly soluble in ether and chloroform, melting at 62° – 64° .

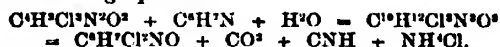
Monacetyl-chloral-ammonia, $\text{Cl}^{\text{H}}\text{C}-\text{CH} \begin{smallmatrix} \text{OH} \\ \text{NH}(\text{C}^{\text{H}}\text{H}^{\text{O}}) \end{smallmatrix}$, formed by the action of acetyl chloride or acetic anhydride on chloral-ammonia, crystallises from hot water in thin rhombic plates which melt at 166° , and are soluble in alcohol, but insoluble in ether.

Diacetyl-chloral-ammonia, $\text{Cl}^{\text{H}}\text{C}-\text{CH} \begin{smallmatrix} \text{OC}^{\text{H}}\text{H}^{\text{O}} \\ \text{NH}(\text{C}^{\text{H}}\text{H}^{\text{O}}) \end{smallmatrix}$ is formed by heating the last compound to 120° in sealed tubes with acetyl chloride, and separates from the resulting solution on cooling as a white crystalline mass, soluble in ether and in glacial acetic acid, and crystallising from the latter in large transparent prisms which melt at 117° – 118° . It is instantly decomposed by water into acetic acid and monacetyl-chloral:



ANILIDE, PHENYLAMIDOCYLORAL, &c.

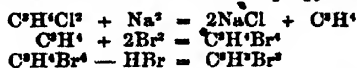
$\text{C}^{\text{H}}\text{H}^{\text{H}}\text{Cl}^{\text{H}}\text{NO} = (\text{C}^{\text{H}}\text{H}^{\text{H}})\text{HN}-\text{CCl}^{\text{H}}-\text{CHO} = \text{NH}(\text{C}^{\text{H}}\text{H}^{\text{H}})(\text{C}^{\text{H}}\text{HCl}^{\text{H}}\text{O})$. Chloral cyanido-cyanate (p. 439) dissolves in aniline with great rise of temperature and evolution of hydrogen cyanide, forming a greasy substance which, on addition of alcohol, solidifies to a crystalline mass consisting of chloral-anilide. The reaction is represented by the following equation:



Chloral-anilide is also formed when aniline hydrochloride is added to a mixture of chloral hydrate and potassium cyanide and cyanate. It dissolves sparingly in water, easily in ether-alcohol, carbon sulphide and glacial acetic acid, and crystallises from the solutions in needles. From a mixture of ether and alcohol it separates in large tabular crystals, which are transparent and colourless at first, but turn red on exposure to the air. These crystals are monoclinic; $a : b : c = 0.8516 : 1 : 0.8967$. Angle $ac = 68^{\circ} 12'$. They are always prismatically developed in the direction of ac , and cleave in the same direction.

Chloral-anilide melts at 117° , gives off when heated the characteristic odour of phenyl isocyanate, but sublimes partly undecomposed in long needles. Hot acids dissolve it, forming solutions from which it crystallises in needles on addition of water. Boiling alkalis convert it into an isonitril (Cech, *Deut. Chem. Ges. Ber.* ix. 337).

CHLORAL, BUTYRIC, $\text{C}^{\text{H}}\text{H}^{\text{H}}\text{Cl}^{\text{H}}\text{O} = \text{CCl}^{\text{H}}.\text{CH}^{\text{H}}.\text{CH}^{\text{H}}.\text{CHO}$ (Pinner, *Liebig's Annalen*, clxxix. 21; *Deut. Chem. Ges. Ber.* viii. 1561). This compound, produced under certain conditions by the action of chlorine on acetaldehyde (2nd Suppl. 35, and p. 50 of this volume), was formerly regarded as crotonic chloral, $\text{C}^{\text{H}}\text{H}^{\text{H}}\text{Cl}^{\text{H}}\text{O}^{\text{H}}$, but has been shown by Pinner's latest researches to have the composition above given. When treated with caustic alkalis it is converted into dichloropropylene or allylene-dichloride, $\text{C}^{\text{H}}\text{H}^{\text{H}}\text{Cl}^{\text{H}}$, and this, when acted upon by sodium, yields allylene, $\text{C}^{\text{H}}\text{H}^{\text{H}}$, which is absorbed by bromine, forming a tetrabromide, and this latter decomposed by potash gives up HBr , and is converted into tribromopropylene:



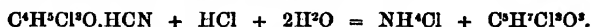
Butyric chloral, dissolved in alcohol and treated with potassium cyanide, yields an ethylic ether boiling at 176° – 178° , which, when heated to 140° – 150° with strong hydrochloric acid, is converted into an acid, said to be monochlorocrotonic acid, $\text{C}^{\text{H}}\text{H}^{\text{H}}\text{Cl}^{\text{H}}\text{O}^{\text{H}}$ (Wallach & Boehringer, *Deut. Chem. Ges. Ber.* vi. 1539); but as the chloral itself has been shown to contain 6 instead of 3 atoms of hydrogen, it is most probable that this acid is really chlorobutyric acid, $\text{C}^{\text{H}}\text{H}^{\text{H}}\text{Cl}^{\text{H}}\text{O}^{\text{H}}$, its formation from butyric chloral being analogous to that of dichloroacetic acid from ordinary chloral.

Compounds of Butyric Chloral.—This compound unites with water, forming a hydrate melting at 78° , and much more readily with alcohol, to form an oily body, which is resolved by distillation into its constituents. The formation of alcoholate takes place even on adding alcohol to the solid hydrate. Butyric chloral combines also with ammonia and organic ammonium-bases; but the compounds thus formed, unlike the fine crystalline bodies obtained with ordinary chloral, are thick, turpentine-like and uncrystallisable. With amides, however, it yields beautifully crystallised products, which are obtained either by boiling an alcoholic solution of butyric chloral, or of the hydrate, with an amide, or better by gently fusing the hydrate with the amide. The compound with acetamide, $\text{C}^{\text{H}}\text{H}^{\text{H}}\text{Cl}^{\text{H}}\text{O}.\text{C}^{\text{H}}\text{H}^{\text{H}}\text{O}.\text{NH}^{\text{H}}$, melts at 170° ; that with

benzamide, $C_6H_5CONH_2$, melts at 150° ; both are soluble in alcohol, but not in water.

Butyric chloral, when boiled with *acetic anhydride*, yields an oil boiling, with partial decomposition, at 240° – 250° . With *acetyl chloride* it combines to form an oily body, distilling at 220° , not decomposable by water at ordinary temperatures, and having the formula $C^4H^3Cl^3O.C^2H^3OCl$.

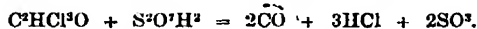
Hydrocyanide of Butyric Chloral, $C^4H^3Cl^3O.HCN = CCl^3-CH^2-CH^2-CHOH-CN$, is formed by adding hydrocyanic acid to an alcoholic solution of butyric chloral. As the hydrocyanide is but slightly soluble, much of it separates as the digestion proceeds, forming a yellow oily layer at the bottom of the flask, and the rest may be obtained by evaporating the supernatant liquid. On cooling, the oil solidifies to a crystalline mass, which may be purified by recrystallisation. It dissolves with difficulty in cold water, more readily in hot water, and still better in alcohol and ether. It melts at 101° – 102° , is less volatile in vapour of water than the corresponding chloral compound (p. 438). It dissolves in hot dilute hydrochloric acid, and crystallises out again unchanged on cooling. By alkalis it is decomposed similarly to the corresponding chloral compound, the products being dichloropropylene, dichlorallylene, formic acid, and hydrocyanic acid. By digestion for a day with concentrated hydrochloric acid the hydrocyanide is converted into trichlorovalerolactic acid, $C^4H^3Cl^3O^2$ (originally supposed to be trichlorangelic acid, $C^4H^3Cl^3O^2$), just as ordinary chloral is converted into trichlorolactic acid, $C^3H^3Cl^3O^2$.



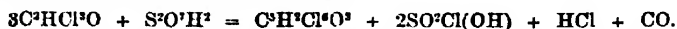
On the bye-products formed in the preparation of Butyric Chloral, see ALDEHYDE (pp. 50, 51).

CHLORAL, HEXOIC, or CAPROIC, $C^6H^3Cl^3O = CCl^3.C^4H^3.CHO$ (Pinner, *Deut. Chem. Ges. Ber.* x. 1052). This compound is obtained by fractional distillation of the higher boiling portions of crude butyric chloral (p. 51), 3 mols. of aldehyde being probably first condensed to form the compound C^6H^3O , which then takes up HCl and Cl^2 to form $C^6H^3Cl^3O$. It boils at 212° – 214° , but has not yet been obtained quite free from butyric chloral. It is insoluble in water, but mixes in all proportions with alcohol, ether, and benzene. It does not form a solid hydrate with water, or a hydrocyanide with prussic acid, but is decomposed by alkaline chlorides yielding a formate and a chloride of alkali-metal, and an organic chloride, $C^6H^3Cl^3$. When mixed with fuming nitric acid it is converted in the course of a few hours into a trichlorocaproic acid, which separates as an oil when the mixture is poured into a considerable quantity of water, and afterwards solidifies. This acid is extremely soluble in alcohol, ether, and benzene, somewhat less soluble in light petroleum, and is precipitated as a fine crystalline powder on adding the latter to a saturated solution of the acid in benzene. It melts at 64° and turns brown at higher temperatures. The melting point of the pure acid would probably be higher. This trichlorocaproic acid is strongly attacked by zinc-dust in presence of water, and if hydrochloric acid be then gradually added, the surface of the zinc becomes covered in a few days with long flat needles of a hexylenic acid, $C^6H^{10}O^2$, melting at 39° . See HEXYLENE COMPOUNDS.

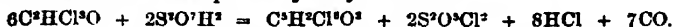
CHLORALIDE, $C^6H^3Cl^3O^2$. This compound is produced by the action of fuming sulphuric acid on chloral or its hydrate. Kekulé prepared it by heating chloral hydrate with an equal volume of fuming sulphuric acid (i. 884). According to Grabowsky, however (*Deut. Chem. Ges. Ber.* viii. 433), this proportion of sulphuric acid is much too large, chloral, when digested in a water bath with an equal volume of fuming sulphuric acid, being wholly resolved into carbon oxide and hydrochloric acid:



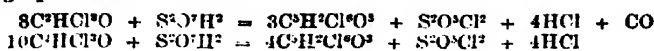
The best proportions for the preparation of chloralide are 1 pt. of fuming sulphuric acid to 3 pts. of chloral, the reaction then taking place as follows, provided the temperature be not allowed to rise above 105° :



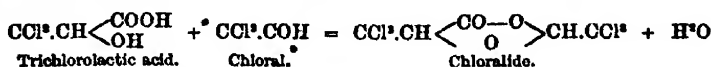
At higher temperatures a somewhat different action occurs, the chloride $S^2O^3Cl^2$ being obtained instead of sulphuric hydroxychloride:



With larger proportions of chloral the substances react in the manner shown by the following equations:



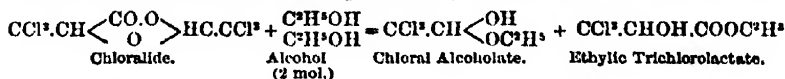
Chloralide is also formed synthetically by heating trichlorolactic acid with anhydrous chloral to 150°–160° for several hours in a sealed tube. This reaction, represented by the following equation, shows that chloralide is the trichlorethidonic ether of trichlorolactic acid:



Lactic acid and chloral under similar conditions yield trichlorethidonic lactate, $\text{CH}^3\text{.CH} \begin{array}{c} \text{CO}_2\text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CH.CCl}^3$ (Wallach u. Heymer, *Deut. Chem. Ges. Ber.* ix. 575).

Chloralide crystallises from alcohol in long prisms having a faint odour which becomes pungent on heating. It melts at 114°–115° and boils at 268° under a pressure of 734 mm. Vapour-density = 11.30 (calc. 11.15). It dissolves in fuming nitric acid at the boiling heat, and crystallises out unaltered on cooling. Heated with water for several days to 200°, it decomposes, with partial carbonisation, and formation of hydrochloric acid, carbon monoxide, and carbon dioxide. Heated to 180° for several hours with aniline, it yields a red mass containing a large quantity of aniline hydrochloride (Grabowsky).

When an alcoholic solution of chloralide is left to itself for some months, or heated for a short time in a sealed tube, it is completely resolved into chloral alcoholate and ethylic trichlorolactate. This reaction, which confirms the view above given of the constitution of chloralide, is represented by the following equation:



(Wallach, *Deut. Chem. Ges. Ber.* viii. 1758).

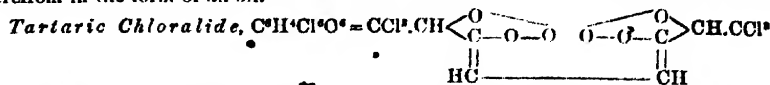
When chloralide is treated with zinc and hydrochloric acid, in presence of alcohol, rise of temperature being prevented as much as possible, aldehyde is formed, together with a fragrant liquid, which, after removal of the alcohol by distillation, and supersaturation with hydrochloric acid, may be dissolved out by agitation with ether, and when freed from ether by evaporation, deposits an abundant crop of crystals consisting of dichloracrylic acid, $\text{C}^2\text{H}^2\text{Cl}^2\text{O}^2$, the mother-liquor retaining others of organic acids, together with other products not yet examined. The formation of aldehyde and dichloracrylic acid may be represented by the equation:



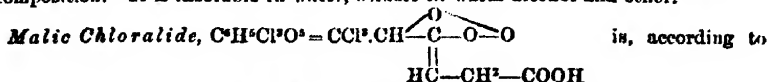
(Wallach, *loc. cit.*)

Compounds analogous to chloralide—trichlorethidonic ethers—are formed by the action of anhydrous chloral on the trichloro-derivatives of various oxy-acids (Wallach u. Hansen, *Deut. Chem. Ges. Ber.* ix. 1214).

Mandelic Chloralide or Trichlorethidonic Mandelate, $\text{C}^6\text{H}^3\text{Cl}^3\text{O}^4 = \text{C}^6\text{H}^3\text{.CH} \begin{array}{c} \text{O} \\ \diagup \\ \text{CO}_2\text{O} \end{array} \text{CH.CCl}^3$, from chloral and mandelic acid, forms small white crystals, melts at 59°, and boils with partial decomposition between 305° and 310°. It is insoluble in water, but dissolves easily in alcohol and ether, and usually separates therefrom in the form of an oil.



crystallises in small needles melting at 122°–124°, and cannot be distilled without decomposition. It is insoluble in water, soluble in warm alcohol and ether.



its composition, a monobasic acid, and reacts as such. It forms fine crystals melting at 137°–138°, dissolves sparingly in cold, easily in hot water, and crystallises therefrom in delicate needles.

CHLORHYDRINIMIDE, $\text{C}^2\text{H}^2\text{Cl}^2\text{N}^2\text{O}^2$. When this compound, formed by the action of ammonia on dichlorhydrin (2nd Suppl. 318) is subjected, in portions of 25 to 30 grams, to dry distillation in small retorts, considerable decomposition takes place, attended with abundant separation of charcoal, and a liquid distils over which separates into two layers, the lower consisting of an aqueous solution of ammonium

chloride and carbonate, while the upper, which is in very small quantity, consists of a dark brown viscid oil. This oil is a base which dissolves in ether and in hydrochloric acid, and from its odour and the character of its platinum double salts, appears to be related to conine and nicotine (Claus a. Dörrenberg, *Deut. Chem. Ges. Ber.* viii. 244).

CHLORIDES. The method described by P. Curie (p. 65) for preparing aluminium chloride, by passing a mixture of hydrochloric acid gas and vapour of carbon sulphide over heated alumina, may be applied to the preparation of other metallic chlorides.

Preparation of the Chlorides of Alkali-metals from the corresponding Sulphates.—When aqueous solutions of an alkaline sulphate and ammonium chloride are evaporated in a porcelain crucible and gently heated, the ammonium chloride may be volatilised without any mutual reaction; but if they are more strongly heated in a platinum crucible, the decomposition is nearly complete after ammonium chloride has been added fourteen to sixteen times. At a low red heat the decomposition is thorough, but at a bright red heat some of the sodium chloride is volatilised. The sodium or potassium chloride should, therefore, not be fused (C. Phillips, *Zeitschr. anal. Chem.* 1874, 149).

Constitution of Hydrochloric Acid and Metallic Chlorides.—J. Thomsen endeavours to show that aqueous hydrochloric acid very probably contains a hydrate of the composition $\text{H}^2\text{O} \cdot \text{HCl}$; that this hydrate must be looked upon as the real acid molecule; and that consequently the chlorides, i.e. the hydrated chlorine-compounds, of the metals, which contain the elements of a molecule of water for every atom of chlorine in them, must be regarded as anhydrous salts of hydrochloric acid.

His investigations are based on:—

(1.) The isomorphism of the hydrated chlorine-compounds with other salts, when the former contain a molecule more of water than the latter for each atom of chlorine in them.

(2.) The specific gravity and specific heat of the aqueous acid.

(3.) The heat-phenomena observed when hydrochloric acid gas is absorbed by water, as well as when the aqueous acid is mixed with water.

For the details of the investigation, see *Pogg. Ann. Jubelband*, 135–149; *Chem. Soc. J.* 1874, 952–959.

A crystallised hydrate of hydrochloric acid, $\text{HCl} \cdot 2\text{H}^2\text{O}$, has been obtained by Pierre a. Puchot (*Compt. rend.* lxxxii. 45). Strong commercial hydrochloric acid may be kept at a very low temperature without any change; but when a continuous current of nearly dry hydrochloric acid gas is passed into the cooled liquid, an abundant deposition of crystals soon occurs, and at the same time the temperature rises from -22° to -18° , remaining stationary at this last point during the formation of the crystals. These crystals decompose rapidly in the air, emitting white fumes; they distil in water very quickly at ordinary temperatures, very slowly at -18° . The synthesis of the hydrate, performed with distilled water, shows that the weight of the separated crystals is about $1\frac{1}{2}$ times that of the water employed, and that the water has taken up about its own weight of hydrochloric acid: hence the formula above given, which is also confirmed by analysis. The form of the crystals has not been exactly determined, but they appear to resemble ordinary soda-crystals.

Purification of Hydrochloric acid from Arsenic.—Instead of the method introduced by Bettendorff (1st *Suppl.* 217), consisting in the use of stannous chloride, H. Hager proposes to dilute the acid to 1.13 sp. gr., then digest it with copper at 80° , and distil. Diez saturates the acid of sp. gr. 1.13 with hydrogen sulphide, and after the precipitated arsenious sulphide has subsided, distils the liquid as long as the distillate smells of hydrogen sulphide (*Chem. Centr.* 1872, 418).

Engel (*Compt. rend.* lxxvi. 1139) adds 4 or 5 grams of potassium hypophosphite to each litre of the acid; the arsenic soon becomes reduced, and when it is all deposited, the clear acid can be decanted and distilled. Potassium hypophosphite may be used as a test for the presence of arsenic in hydrochloric acid, the reduction taking place immediately on the application of heat. Hager (*Chem. Centr.* 1874, 98) adds 0.4 to 0.5 grm. potassium or sodium hypophosphite to 100 grams of the acid, and after gentle warming, whereby the arsenic is precipitated, filters the liquid through sand; a small quantity of potassium chlorate is then added, and after the lapse of a day, the slight excess of free chlorine is removed by digestion with strips of copper.

To detect arsenic in hydrochloric acid, J. B. Oster (*Zeitschr. anal. Chem.* xi. 463) boils the acid with strips of tin-foil, and leaves the liquid to cool. A trace of arsenic colours the liquid and stains the tin. It must be observed, however, that a similar appearance is produced by the presence of ferric chloride.

Preparation of Alcoholic Chlorides.—The chlorides of methyl and ethyl are easily prepared in considerable quantity by dissolving 1 pt. of zinc chloride in 2 pts. of the corresponding alcohol, and boiling the solution in a flask provided with reflux apparatus, while a stream of hydrochloric acid gas is kept passing through it. The alcoholic chloride which passes over is purified by washing with water. Amyl chloride may be prepared in a similar manner (Groves, *Chem. Soc. J.* 1874, 636).

Schorlemmer (*ibid.* 1875, 308) finds that the method is not applicable to the preparation of the chlorides of the higher alcohols. Primary heptyl alcohol, treated as above, yielded a mixture of primary and secondary heptyl chlorides together with heptylene, and a high-boiling liquid, probably consisting of condensed heptylenes or diheptylic ether, or a mixture of both. Amyl alcohol, treated in like manner, also yielded a mixture of primary and secondary amyl chloride.

Preparation of the Chlorides of Acid Radicals.—These chlorides are usually prepared by treating the fatty acids with trichloride or pentachloride of phosphorus; but as the preparation of these phosphorus chlorides is difficult and costly, Kannonnikoff (*Liebigs Annalen*, clxxv. 378) proposes to replace them by the oxychloride POCl_3 , which occurs as a bye-product in many reactions. By treating acetic acid with the oxychloride, and fractionating the product, he obtained nearly pure chloride of acetyl: butyric acid treated in like manner yielded butyryl chloride: succinic acid, however, yielded, not succinyl chloride but succinic anhydride.

CHLORINE. On Deacon's method of preparing Chlorine, and the causes which interfere with its success, see Hasenclever (*Deut. Chem. Ges. Ber.* 1874, 2; *Dingl. pol. J.* cxxi. 195; *Jahresb. f. Chem.* 1874, 1098); Lunge (*Deut. Chem. Ges. Ber.* 1874, 1526; *Jahresb.* 1874, 1111); Jurisch, (*Dingl. pol. J.* cxxxi. 356, 448; cxxii. 366; *Jahresb.* 1876, 1081; *Chem. Soc. J.* 1877, i. 350).

According to Lamy (*Bull. Soc. Chim.* [2], xx. 2), all compounds of copper, iron, manganese, and chromium, also porcelain, pumice, silica, glass (all of which probably contain traces of the elements just mentioned) are capable, when a stream of hydrochloric acid gas and air is passed over them at high temperatures, of inducing the oxidation of the hydrochloric acid to water and chlorine, the quantity of free chlorine thus obtained depending on the conditions pointed out by Deacon. With copper the most suitable temperature is 440° ; with compounds of manganese, iron, and chromium, higher temperatures. Pumice, glass, and porcelain, give less chlorine the purer they are; thus crude pumice gives 15 per cent. chlorine at 440° , 30 per cent. at a red heat; purified pumice much less.

De Lalonde a. Prudhomme, on the other hand (*Bull. Soc. Chim.* [2], xx. 74), are of opinion that the decomposition of hydrochloric acid which takes place on passing that gas mixed with air over heated mixtures of alkaline chlorides with boric oxide, silica, &c. (*2nd Suppl.* 321), does not depend on the contamination of those bodies with ferric salts, &c., but that the alkaline chlorides are converted by the oxygen of the air at a red heat into oxides, with evolution of chlorine, the oxides being then reconverted into chlorides by the actions of the hydrochloric acid, so that a continuous evolution of chlorine takes place.

Tessie du Mothay's Method.—A stream of hydrochloric acid gas is passed into a retort containing manganese dioxide and chalk, kept at a dull red heat, whereby chlorine and watery vapour are evolved; and the chlorine is passed into water, or into a chamber where dry hypochlorites are to be prepared. A stream of air being now passed over the residue in the retort at the same temperature, the chlorine which had gone to form calcium chloride (or manganous chloride) is set free, and is conducted (mixed with air as it is) into stoneware vessels containing chalk and manganous oxide suspended in water; manganic oxide and calcium hypochlorite are thus produced, together with calcium chloride. This mixture treated with hydrochloric acid evolves pure chlorine. The residue in the vessel (manganous chloride and calcium chloride) heated with excess of lime, and freed from calcium chloride by washing, gives again the original mixture of manganous oxide and lime, into which fresh supplies of chlorine mixed with air may be conducted.

The calcium chloride is transformed by the action of magnesium carbonate into magnesium chloride (which again yields hydrochloric acid) and calcium carbonate. The chlorine produced by this method is said to be very pure (*Dingl. pol. J.* ccv. 359).

An apparatus for the evolution of chlorine on the laboratory scale is described by A. Orlewsky (*Zeitschr. anal. Chem.* 1872, 38; *Chem. Soc. J.* 1872, 96).

Purification.—To purify chlorine gas from hydrochloric acid, which always accompanies it when prepared by the ordinary methods, F. Stolla (*Chem. Centr.* 1874, 116) washes the gas with a tolerably concentrated solution of cupric sulphate, and finally with water. The chlorine is made to pass over the copper solution as slowly as

possible, and into the solution are thrown numerous pieces of pumice-stone, which float, thus affording a large surface. A cupric sulphate solution has a great tendency to absorb hydrochloric acid, cupric chloride being formed and sulphurous acid liberated. The chlorine passes on unaffected.

Estimation.—According to R. Messel (*Zeitschr. anal. Chem.* 1876, 123), the estimation of chlorine or hydrochloric acid by means of a standard silver solution, with potassium chromate as an indicator (Mohr's method), cannot be applied if sulphurous acid is present, since the final reaction does not take place till the whole of the sulphurous acid has been precipitated as silver sulphite. According to G. Lunge, however (*ibid.* 424), if the sulphurous acid be previously oxidised to sulphuric acid by means of permanganate solution, Mohr's method may be applied without diminution of the sharpness of the reaction.

As potassium chromate is often contaminated with chlorides, A. R. Leeds (*Amer. Chemist*, 1873, 453) recommends that in performing a number of comparative analyses by the above method, the chromate should be added always in the same volume.

Stolba (*Chem. Centr.* 1874, 122) recommends *potassio-calcic chromate* as an indicator in Mohr's method. To prepare it, potassium dichromate, freed from all traces of chlorine by recrystallisation, is dissolved in eight times its weight of water and heated to boiling. To the hot solution well-washed calcium hydrate is added, till the solution has attained a pure yellow colour, and in consequence of excess of lime a pellicle or skin of calcium carbonate is formed on the surface of the liquid when blown upon. The hot solution is filtered, and concentrated by slow evaporation, whereby the excess of lime is separated as carbonate; or carbon dioxide may be passed through the hot solution, in which case great care must be taken to wash the gas thoroughly. The decanted solution is ready for use.

On Böhlig's Volumetric Method, see *Arch. Pharm.* [3], iii, 122; *Chem. Soc. J.* 1874, 815.

Chlorine Hydrate. This compound, formed by the action of chlorine on water at 0°, is regarded sometimes as $\text{Cl}^2 \cdot 10\text{H}^2\text{O}$, sometimes as $\text{HOCl} \cdot \text{HCl} \cdot 9\text{H}^2\text{O}$. On the former supposition, the hydrate, when treated with mercury, should yield mercurous chloride, just as free chlorine does. It has, however, been shown by Gépner (*Deut. Chem. Ges. Ber.* viii, 287), that the product formed in this reaction is chiefly mercuric chloride, a small portion only of this compound being reduced to mercurous chloride by the excess of mercury present. This result is in favour of the latter view of the composition of chlorine hydrate, the mercury being supposed in the first instance to act upon the hypochlorous acid in the molecule, forming mercuric oxychloride:



which is then converted by the hydrochloric acid into mercuric chloride. On this view the action of chlorine on water at 0° may be regarded as analogous to that which it exerts on the alkaline hydrates:



On the other hand, Hugo Schiff (*ibid.* 419) points out that the supposition of part of the chlorine being contained in the hydrate as hypochlorous acid is inconsistent with the following facts: (1). A saturated solution of hypochlorous acid is quickly decomposed by light, whereas chlorine hydrate, which contains nearly the same amount of chlorine, remains unaltered. (2). The hydrate does not corrode or discolour the epidermis as it should do if it contained free hypochlorous acid; and, as shown by Faraday, it acts on organic substances in general just like free chlorine. (3). As neither HClO nor HCl by itself forms a definite hydrate, it is not probable that these compounds can exist as such in the hydrate of chlorine.

There are, however, two facts which seem to indicate that the hydrate does not contain free unaltered chlorine, viz. (a) that in the dry state, notwithstanding its large amount of chlorine, its odour is much fainter than that of saturated chlorine-water containing only 0.7 per cent. chlorine; this, however, may perhaps be due to the lower tension of the chlorine contained in the hydrate; (b) that it has but a faint colour, whereas in most cases compounds of coloured bodies with water of crystallisation are more deeply coloured than the same compounds in the anhydrous state (Schiff).

Oxides and Oxygen-acids.

Oxide, Acid, and Salts. When phosphorus oxychloride is added by drops to *potassium chlorite*, a yellow-green gas is given off, which is absorbed in large quantity by water or potash, forming hypochlorous acid or potassium hypochlorite.

When *chlorous acid*, ClO^2 , is passed over phosphorus pentachloride, hypochlorous acid, ClO , is formed often with violent explosion (W. Spring, *Dent. Chem. Ber.* 1874, 1684).

Hypochlorous acid is also formed when oxygenated water (containing 2.45 per cent. O_2) is added to a large excess of chlorine-water: $\text{Cl}^2 + \text{H}^2\text{O}^2 = 2\text{HClO}$. With a large quantity of hydrogen dioxide, oxygen is formed at the same time:



Hypochlorous acid and its salts are converted by *ozone* into perchloric acid and perchlorates (Fairley, *Jahresb. f. Chem.* 1874, 210).

Detection and Estimation of Hypochlorous acid in presence of Chlorine, Chlorous acid, and Chloric acid.—Free hypochlorous acid agitated with metallic mercury converts it into mercuric oxychloride, $\text{Hg}^2\text{Cl}^2\text{O}$ or $\text{HgCl}^2.\text{HgO}$, whereas free chlorine converts mercury into mercurous chloride, Hg^2Cl^2 . Consequently, hypochlorous acid mixed with chlorine may be easily detected by the more yellowish colour produced on shaking it with mercury, unless its quantity is very small in comparison with the free chlorine. In the latter case it is necessary to decompose the oxychloride with hydrochloric acid, filter, and agitate the filtrate with mercury. If the hypochlorous acid is in combination with bases, its detection is even easier than in the free state; for in this case, agitation with mercury gives rise to the yellow oxide, easily recognised by its colour, and by its property of sticking to the sides of the glass vessel on agitation: $\text{KClO} + \text{Hg} = \text{HgO} + \text{KCl}$. Chlorous and chloric acids when combined with bases do not act upon mercury (Wolters, *J. pr. Chem.* [2], vii. 468).

These reactions may be made the basis of a quantitative estimation of hypochlorous acid in presence of free chlorine, chlorites, and chlorates, inasmuch as by brisk agitation with excess of mercury, the whole of the hypochlorous acid and its salts may be decomposed in about five minutes. The mercuric oxide formed in the reaction is easily dissolved by hydrochloric acid; the mercury contained in the filtrate may be precipitated as mercurous chloride by ferrous salt and an alkali; and the quantity of mercury thus precipitated gives by calculation the quantity of hypochlorous acid present, 1 atom of mercury answering to 2 molecules of hypochlorous acid (HClO), or to 2 atoms of active chlorine in bleaching powder:



Free chlorine does not interfere with the estimation, since the mercurous chloride formed by its action on the mercury remains undissolved on addition of hydrochloric acid, and may be separated by filtration together with the excess of mercury. Chlorites and chlorates remain in the filtrate after agitation with mercury, and may be converted into mercurous chloride by agitation with mercury and hydrochloric acid.

The method of analysis is therefore as follows: The solution is shaken for some minutes with excess of metallic mercury, and the chlorates and chlorites are filtered off, leaving a mixture of mercuric oxide, mercurous chloride, and finely divided mercury. This mixture is exhausted with hydrochloric acid, which dissolves only the mercuric oxide, and the mercury is precipitated from the filtrate as mercurous chloride by a ferrous salt and alkali, and after addition of acid is dried and weighed. Estimations of active chlorine in bleaching powder made in this manner agree well with those made with ferrous sulphate (Wolters).

Calcium Hypochlorite.—This salt may be separated from bleaching powder in feathery crystals, having the composition $\text{CaCl}^2\text{O}^2 + 4\text{H}^2\text{O}$, by exposing the filtered solution of the powder to a freezing mixture, or by evaporating it in a vacuum over sulphuric acid (Kingzett). See BLEACHING POWDER, p. 383.

Chlorate Acid, HClO^3 . A method of estimating this acid, founded on the reduction of chlorates to chlorides by nascent hydrogen, is given by T. E. Thorpe (*Chem. Soc. J.* 1873, 541). The reduction is effected by means of zinc-foil which has been coated with finely divided copper by immersion in solution of cupric sulphate (Gladstone's copper-zinc couple).

Chlorates may be conveniently pulverised for pyrotechnical purposes by immersing pieces of glass in a hot saturated solution of the salt. A fine deposit is then formed on the glass, which may be scraped off with a card (Gawalowski, *J. pr. Chem.* [2], ix. 240).

From experiments by G. Schacherl (*Liebig's Annalen*, clxxxii. 193) it appears that the action of hydrochloric acid on potassium chlorate, or of sulphuric acid on a mixture of the chlorate and chloride, does not give rise to the formation of perchloric acid, but takes place according to the following equation:



The evolution of larger quantities of chlorine hitherto observed is due to a secondary action of the hydrochloric acid on the chlorine tetroxide. Pure chlorine gas is never obtained by the action of hydrochloric acid on potassium chlorate, the secondary action just spoken of being never complete.

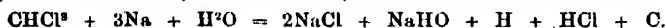
Perechlorates. The solubility of potassium perchlorate in water has been determined by Muir (*Chem. News*, xxxiii. 15), with the following results:

Temperature.	Percentage of salt in solution.	Sp. gr. of solution.	Quantity of water required for 1 pt. KClO_4 .
0°	0.705	1.0005	142.9
25°	1.92	1.0123	52.5
50°	5.07	1.0181	15.4
100°	15.76	1.06603	5.04

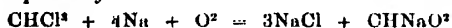
Bismuth Perchlorate, BiOClO_4 , is obtained by heating metallic bismuth with aqueous perchloric acid, as a white amorphous powder, insoluble in water, easily soluble in hydrochloric and nitric acids, less soluble in sulphuric acid; decomposed at a red heat, with formation of bismuth trichloride (Muir, *loc. cit.*)

CHLORITE. Pseudomorphs of chlorite after garnet are found in all stages of transformation, in a chlorite-slate of the Spurr-Mountain iron mine, near Lake Superior (R. Pumpelly, *Sill. Am. J.* [3], x. 17).

CHLOROFORM, CHCl_3 . *Action of Sodium.*—When chloroform is treated with sodium and a small quantity of water, hydrogen and hydrochloric acid are quickly evolved, while caustic soda, sodium chloride, and carbon remain in the tube:

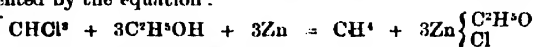


When chloroform and sodium were left together for several days in a loosely covered test-tube, sodium formate was precipitated as a brown substance, which, when dried over sulphuric acid, became somewhat crystalline, and whitened on exposure to the air. The reaction is probably:



(S. Kern, *Chem. News*, xxxi. 121).

Action of the Copper-zinc Couple.—The dry couple does not act on chloroform either alone or in presence of pure ether. In presence of absolute alcohol, no action is observed at ordinary temperatures, but at 50°–60° marsh-gas is evolved, together with a small quantity of acetylene, and chloroethylate of zinc remains in the vessel. The relative quantities of these products show that about 92 per cent. of the action may be represented by the equation:



and a small proportion by the equation:



In presence of water, reaction begins at 12° with slow evolution of gas, the temperature then rising and the evolution becoming more rapid, the action being completed in about four days. Zinc oxychloride is produced, which forms a white coating on the couple, and the gas burns with a blue flame, like that of marsh-gas. Hence it is inferred that the action takes place in the manner represented by the equation:



With aqueous alcohol the action takes place at a lower temperature than with absolute alcohol, and is likewise attended with formation of zinc oxychloride.

Zinc-foil has no action on chloroform mixed with absolute alcohol at 60°, but at the boiling point of the mixture there is a slow action, CH^4 and $\text{C}^2\text{H}_5\text{O} \left\{ \begin{array}{l} \text{C}^2\text{H}_5\text{O} \\ \text{Cl} \end{array} \right\} \text{Zn}$ being produced.

Zinc-foil was also found to act slowly upon chloroform mixed with alcohol diluted with one fourth of its volume of water at 50°, zinc oxychloride and CH^4 being the principal products.

The reactions described above afford a ready method of preparing marsh-gas (Gladstone & Tribe, *Chem. Soc. J.* 1875, 508).

Action of Antimony Pentachloride.—Chloroform heated with this compound in a reflux apparatus or to 100° in a sealed tube, is converted into carbon tetrachloride, with formation of antimony trichloride and hydrochloric acid: $\text{CHCl}_3 + \text{SbCl}_5 = \text{CCl}_4 + \text{SbCl}_3 + \text{HCl}$ (Lössner, *J. pr. Chem.* [2], xiii. 418).

Action of Potassium Phenate.—When an alcoholic solution of phenol mixed with caustic potash is evaporated to dryness, and chloroform is poured upon the residue

while still hot, a splendid red-purple colour is immediately produced. The potash should not be in excess, and the temperature not very high. This reaction is capable of detecting 0.1 mgm. of phenol.

The coloration is probably due to the formation of rosolic acid, which is, in fact, known to be produced by the action of iodoform, formic acid, &c., on potassium phenate.

The action of potassium phenate on chloroform does not give rise to any compound analogous to the triethylic formate or orthoformic ether, which Kny obtained by treating chloroform with sodium ethylate (Guareschi, *Gazz. chim. ital.* 1873, 401).

Action on Sodacetic Ether. See ACETO-ACETIC ETHERS (p. 17).

Preparation.—Hartsen (*Chém. Centr.* 1873, 204) prepares pure chlorophyll by making finely chopped ivy leaves into a paste with spirit of 55°, and pressing the paste after twelve hours. This removes the water, a bitter substance (*helicin*), and a saponifiable compound. The pressed leaves are now soaked in benzene for twenty-four hours, and the benzene is removed from the expressed solution by distillation. The dark brown fatty residue, amounting to 2½ per cent. of the leaves, is treated with a solution of sodium hydrate, filtered, and precipitated by common salt. The precipitate, after being washed with a salt solution, is dissolved in water, and precipitated with a solution of copper sulphate. This precipitate, after being washed and dried, is boiled with absolute alcohol, and then washed with ether and benzene; this treatment removes the copper soap, and leaves the compound of chlorophyll with copper oxide. Finally, the latter is suspended in alcohol, and decomposed by sulphuretted hydrogen. On evaporating the solution, the chlorophyll is left of a very dark green colour, almost black, and quite free from fatty matter. It is soluble in hydrochloric acid and in alcohol, yielding a solution of a very fine green colour.

Spectrum.—The absorption-spectrum of chlorophyll is characterised by a certain number of bands, among which is one at the red end which suffices to distinguish chlorophyll under all circumstances, and exhibits the following characters:

- a. *Sensibility*: having a clear outline, a fixed position, and remarkable permanence, even in a solution diluted to the one-ten-thousandth.
- b. *Certainty*: being divided into two lines, under the influence of alkalis, a character which does not belong to the rays of blood, bile, or any other organic liquid.
- c. *Constancy*: being always present wherever there is chlorophyll, either pure or altered.

Chlorophyll can be perfectly recognised by the spectroscope, whether it has been obtained from young leaves, old leaves, or dead leaves which have been subject to the action of light and air.

- a. In young leaves, by *temporary accidental bands*, developed under the action of hydrochloric acid.
- b. In old leaves, by a *permanent accidental band*, developed in an alcoholic solution with the same acid.
- c. In dead leaves, by *permanent accidental bands*, which appear immediately in the alcoholic solution without the intervention of hydrochloric acid.

Chlorophyll is much less alterable than is generally supposed; it resists the action of iodine, acids, alkalis, and the animal digestive powers, and preserves, under the influence of these agents, if not its composition and primitive character, at least some properties which permit of its recognition in the most complex and varied mixtures, even after a considerable lapse of time (Chautard, *Compt. rend.* lxxvi. 1273; lxxvii. 596; *Ann. Chim. Phys.* [5], iii. 2-56).

Alteration of Chlorophyll by the action of Light.—An alcoholic solution of chlorophyll becomes decolorised when exposed to the magnesium light for half an hour, even when it is protected from the heat by being surrounded with a stratum of water. Sensitive photographic paper exposed in a similar manner for the same time, side by side with the chlorophyll solution under a stratum of a solution of potassium dichromate, is scarcely acted on, whilst the chlorophyll solution is decolorised. On the contrary, when copper sulphate is substituted for the dichromate, the paper is blackened, but the chlorophyll solution remains unchanged (A. Cossá, *Deut. Chem. Ges. Ber.* vii. 358).

Chautard finds that the action of light on chlorophyll is considerably modified by the nature of the solvent. Thus when chlorophyll is dissolved in fixed oils, the colour undergoes no alteration in full daylight in eight or ten months. In benzene the alterability of chlorophyll under the action of light is rather quick, but far less so than in presence of alcohol.

If to an alcoholic solution there be added a drop or two of potash, the green colour becomes more persistent, at the same time that the red band doubles itself after some time, as it does immediately under the influence of heat. The same doubling takes place under the prolonged action of ammonium sulphhydrate, but it requires several months keeping in a dark place to produce the effect. An alcoholic solution of cabbage chlorophyll, treated with a little ammonia, likewise develops these supernumerary bands, which always appear in the portion of the spectrum more refrangible than the red (*Compt. rend.* lxxviii. 414).

The brightest rays of the spectrum not only cause the largest amount of assimilation in plants, but are likewise most effective in bringing about the formation and destruction of chlorophyll. The less refrangible part of the spectrum is not, however, as hitherto supposed, capable of producing all the chemical actions which take place in the chlorophyll granules; this is true indeed with regard to the formation and oxidation of chlorophyll, and the assimilation of carbonic acid and water; but the oxidation of xanthophyll takes place only under the influence of the most refrangible or chemical rays. The brightness of light, under whose influence the green substance is formed, is much less than that required for the destruction of chlorophyll; but the brightness necessary for oxidation of chlorophyll is the same as that required for the assimilation of carbonic acid and water in the chlorophyll granule.

Solutions of chlorophyll and xanthophyll remain unaltered in a dark room, even if exposed to ordinary (inactive) oxygen, but they are bleached on exposure to light. If, however, chlorophyll be dissolved in turpentine-oil containing active oxygen in solution, decoloration will take place even in the dark.

The fact that in light of high intensity more chlorophyll is destroyed than is formed, explains the phenomenon that etiolated plants become green more rapidly in diffused light than in direct sunshine, and that plants of a bright green colour become paler in very bright light, and recover their deep green colour under moderate illumination (*Wiesner, Chem. Centr.* 1874, 353).

Action of Hydrochloric acid.—Solutions of chlorophyll in presence of hydrochloric acid undergo a remarkable decomposition; the green colour disappears; the liquid becomes turbid; and on filtration, a solid matter, nearly black, remains on the filter. This black matter, when dicotyledonous plants have been used, is amorphous; whereas that obtained from the chlorophyll of monocotyledonous plants is crystalline. It is soluble in ether, benzene, chloroform, carbon sulphide, and in boiling alcohol of 5 per cent. The colour of the solution varies with the solvent, being brownish-yellow with ether and benzene; yellow with carbon sulphide; and violet with chloroform. All the solutions give a spectrum having five absorption-bands similar to those produced by chlorophyll, but not occupying the same position in the spectrum, and varying a little according to the nature of the solvent. Prolonged exposure to solar light decolorises the solution (*Filhol, Compt. rend.* lxxix. 612; *J. Pharm. Chim.* [4], xx. 345).

Constitution.—Frémy, from experiments made some years ago, concluded that chlorophyll is a compound of a blue substance, phyllocyanic acid, and a yellow substance, phylloxanthin, the former being soluble in hydrochloric acid, the latter in ether (*1st Suppl.* 443). By more recent experiments (*Compt. rend.* lxxxiv. 983), he finds that the phylloxanthin may be extracted from chlorophyll by alcohol of 62 per cent., which leaves the phyllocyanic acid undissolved; this latter is, however, dissolved by alcohol of 70 per cent. On adding a few drops of baryta-water to an alcoholic solution of chlorophyll, a deep green barium salt of phyllocyanic acid is precipitated, while the alcohol acquires a fine golden-yellow colour from the phylloxanthin which remains in solution. Frémy is of opinion that the yellow and blue substance exist in chlorophyll in a state of simple mixture. The green colouring matter contains potash, and may therefore be regarded as phyllocyanate of potassium; and, in fact, by decomposing the phyllocyanate of barium with a solution of potassium sulphate, a phyllocyanate of potassium is obtained, which dissolves in alcohol with a fine green colour, and agrees in its spectroscopic and other characters with the green colouring matter extracted from leaves by alcohol.

The constitution of chlorophyll has also been investigated by Leo Liebermann (*Wien. Acad. Ber.* [2te Abth.] lxxii. 599), by means of spectroscopic observations on solutions of chlorophyll, on a decomposition-product obtained by treating chlorophyll with hydrochloric acid, and on alcoholic extract of violets previously treated with nitric acid and then with ammonium sulphide. These observations lead to the following conclusions: (1.) The chlorophyll of different plants exhibits but trifling differences in optical characters, and consists in all cases of a saline compound, composed of chlorophylllic acid and a basic substance. (2.) The basic component, phyllochromogen, is capable of assuming the most various colours under the influence of

oxidising and reducing agents, and is in fact the parent of the colouring matters of flowers. (3.) The formation of the colouring matters of flowers may be explained on the supposition that the chlorophyll is in some way resolved into the two constituents above mentioned, and that the phyllochromogen is converted by oxidation into a violet, blue, or red colouring matter. (4.) When the leaves fade, a slight reduction of the chlorophyll takes place. (5.) The basic constituent of chlorophyll and the colouring matters of flowers, are in some respects analogous to the colouring matter of blood, exhibiting an absorption-spectrum similar to that of oxyhæmoglobin; moreover, chlorophyll is said to contain iron, and, like hæmatin, is dichroic in alcoholic or alkaline solutions.

See further, Pringsheim (*Chem. Centr.* 1876, 217); and Sachsse (*Sitzungsber. d. naturforsch. Gesellsch. in Leipzig*, 1876, 115; *Jahresb. f. Chem.* 1876, 871, 872; *Chem. Soc. J.* 1877, ii. 208).

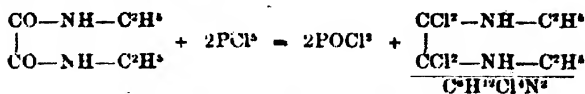
Assimilative Function of Chlorophyll.—Sachsse (*loc. cit.*) regards chlorophyll as the first visible assimilation-product of the vegetable organism, and supposes that it is formed by reduction of carbon dioxide and water; that by further alteration and reduction it is converted into starch, and other carbohydrates, and consequently that chlorophyll is the mother-substance of starch.

According to Briosi (*Gazzetta chimica italiana*, 1876, 457), starch is never found in the chlorophyll grains of vine-leaves; fatty matters and glucose also are present only in insignificant quantities, whilst tannin is abundant, being found, not only in the epidermal cells, but also in those containing chlorophyll, and most largely in the upper layers of the leaf exposed to the direct action of light, where the action of the chlorophyll is most energetic. Briosi does not, however, consider this fact, even when taken in conjunction with other unpublished observations, sufficient to warrant the conclusion that the tannin is formed in the chlorophyll of the vine-leaves, as the researches hitherto made on the function of tannin indicate that it is a secondary product, or product of degradation.

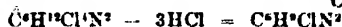
On the Assimilative Function of Chlorophyll, see also Gerland (*Pogg. Ann.* cxlviii. 99; *Chem. Soc. J.* 1873, 401); Stutzer (*Deut. Chem. Ges. Ber.* ix. 1395; *Jahresb. f. Chem.* 1876, 864); Krauss (*Z. Arch. pl. nat.* lv. 335; *Jahresb.* 1876, 864).

On the existence of Chlorophyll in the undigested residues of Food, see Chautard (*Compt. rend.* lxxvi. 103; *Chem. Soc. J.* 1873, 521).

CHLOROXAETHYLENE, $C^2H^2ClN^2$ (Wallach, *Deut. Chem. Ges. Ber.* vii. 326; *Liebig's Annalen*, clxxiv. 1). A base produced by the action of phosphorus pentachloride (2 mol.) on diethyloxamide (1 mol.) On mixing the two substances, reaction begins immediately, with evolution of hydrochloric acid, and a light yellow liquid is formed, from which diethyloxamide may be reproduced by the action of water, but which, when left to itself, decomposes spontaneously, with rise of temperature, and further evolution of hydrochloric acid. On freeing this liquid by distillation under reduced pressure, from the phosphorus oxychloride produced in the reaction, the chloroxaethylene remains in the form of hydrochloride. The reaction appears therefore to take place by two stages:



and



Chloroxaethylene is a transparent colourless oily liquid, having a narcotic odour and strong alkaline reaction, a sp. gr. of 1.1420 at 15°, and boiling constantly at 217°-218°. It is combustible; attacks caoutchouc strongly; crystallises in a freezing mixture; and dissolves in alcohol, ether, and a large quantity of water, but is less soluble in warm water than in cold, so that a clear solution prepared at ordinary temperature becomes turbid even at the heat of the hand; conine exhibits the same peculiarity. The aqueous solution has a bitter taste. The base itself acts like a nerve-poison.

Chloroxaethylene is a strong base. Its salts dissolve very easily in water and in alcohol, and crystallise well. The *hydrochloride*, $C^2H^2ClN^2.HCl$, crystallises from an aqueous solution in needles containing 1 mol. of water. On standing over sulphuric acid it becomes anhydrous, and is converted into a crystalline, very hygroscopic mass. From alcohol it crystallises in prisms; it sublimes readily, and can be distilled without decomposition. The *platinchloride*, $(C^2H^2ClN^2.HCl)_2PtCl^4$, crystallises from

dilute alcohol in well-defined prisms. The *nitrate* and *sulphate* dry up to viscid mass. The *oxalate*, $C^8H^8ClN^2.C^2O^4H^2$, is obtained in white needles by adding ether to alcoholic solution of the base and oxalic acid. The *picrate* forms yellow needles.

With *metallic salts* chloroxalethyline forms a series of well-characterised double compounds and precipitates. *Silver nitrate* forms in the aqueous solution of the base a precipitate of the compound $C^8H^8ClN^2.NO^3Ag$, which crystallises from water in long needles, from alcohol in thick prisms. With *mercuric chloride* two compounds are formed, viz. $C^8H^8ClN^2.HgCl^2$, produced like the silver salt, crystallising in needles, slightly soluble in water and in alcohol, melting at 100° ; and $C^8H^8ClN^2.HCl.4HgCl^2$, which is formed on adding mercuric chloride to a solution of chloroxalethyline hydrochloride, and crystallises in needles very soluble in hot water. A very finely crystallised compound is also formed with mercuric cyanide.

An aqueous solution of the base yields also the following precipitates:

Mercurous nitrate: white, voluminous.	Ferric chloride: brown.
Mercuric cyanide: white, crystalline.	Ferrous sulphate: bluish green.
Stannous chloride: white.	Cobalt nitrate: violet.
Auric chloride: yellowish brown.	Iodine and potassium iodide: brown.
Copper sulphate: after some time or on heating, blue.	Potassio-mercuric iodide: white.
Thallium chloride: white, soon turning brown.	Phosphomolybdic acid: yellow.
	Ammonium molybdate: white.
	Tannin: white.

Bromine unites with chloroxalethyline in ethereal solution, without perceptible evolution of hydrobromic acid, forming an addition-product which solidifies in deep-red crystals.

With the *alcoholic iodides, bromides, &c.*, chloroxalethyline reacts like a tertiary base, producing compounds of the ammonium type. With methyl iodide, a violent reaction soon sets in, the compound $C^8H^8ClN^2.CH^3I$ being formed, which crystallises in white prisms or needles. On boiling this iodide with caustic potash, ethylamine is given off. The iodide, treated with an alcoholic solution of iodine, yields a crystalline periodide; it also forms a similar compound with bromine. On treating the iodide with moist silver oxide, the very alkaline hydroxide, $C^8H^8ClN^2.C^2H^3(OH)$, is formed, crystallising in deliquescent plates. $C^8H^8ClN^2.C^2H^3Br$ is formed only when its constituents are heated together to 100° , and crystallises in very hygroscopic needles; the perbromide forms beautiful crystals.

In all the reactions above described chloroxalethyline exhibits a close analogy to the alkaloids of the nicotine group.

CHLOROALMETHYLIN, $C^8H^8ClN^2$, is formed, like the ethyl-compound, by the action of phosphorus pentachloride on dimethyloxamide, and may be obtained in the pure state by distilling off the phosphorus oxychloride, dissolving the residue in cold water, adding potash, shaking with chloroform, and distilling the crude base which remains on volatilising the chloroform over baryta.

Chloroxalethyline thus prepared is a colourless liquid, boiling at 204° – 205° . It is miscible with water in all proportions, has a strongly alkaline reaction, and yields with dilute sulphuric acid a solution, showing a fine fluorescence. It has an unpleasant, sweetish smell, and a caustic, bitter taste. The *hydrochloride*, $C^8H^8ClN^2.HCl + H^2O$, is very soluble in water and alcohol, and forms oblique prisms, which are stable in air, lose their water over sulphuric acid, and then become deliquescent. The *platinochloride*, $(C^8H^8ClN^2.HCl)^2PtCl^4$, crystallises from water or dilute alcohol in long reddish-yellow needles, which are almost insoluble in absolute alcohol. The *oxalate*, $C^8H^8ClN^2.C^2O^4H^2$, is much less soluble than the corresponding chloroxalethyline salt, and crystallises from alcohol in prisms. The *picrate* forms small yellow needles. The base gives precipitates with metallic salts.

The *methiodide*, $C^8H^8ClN^2.CH^3I$, crystallises from alcohol in white needles, and yields a periodide forming deep-red needles, and a perbromide crystallising in yellow plates (Wallach, *loc. cit.*)

CHOLESTERIN, $C^{26}H^{44}O$. *Density*.—According to Méhu (*J. Pharm. Chim.* [4], xx. 175), the density of cholesterol (referred to water at 20° as unity) is 1.046–1.047; according to Hoppe-Seyler (*Gmelin's Handbook*, xviii. 113) it is 1.067; according to Hein (*ibid.*) it is 1.03, after fusion.

Reaction with Sulphuric acid.—When sulphuric acid is added to a solution of cholesterol in chloroform, the upper liquid assumes a blood-red or purple-red colour, while the under liquid exhibits a green fluorescence (E. Salkowski, *Chem. Centr.* 1873, 285).

Oxidation.—The oxidation of cholesterol by potassium permanganate yields three acids, viz. cholesteric acid, $C^{26}H^{40}O^4$, oxycholesteric acid, $C^{26}H^{38}O^4$, and dioxycholesteric acid, $C^{26}H^{36}O^4$. These acids are soluble in ammonia and form amorphous precipitates with all metals, except the alkali-metals. They are separated by means of their salts; those of dioxycholesteric acid dissolve in benzoin (petroleum), but are insoluble in alcohol and ether; those of oxycholesteric acid dissolve in benzoin and in ether; those of cholesteric acid in alcohol, ether, and benzoin (Latschinoff, *Bull. Soc. Chim.* [2], xxvii, 456).

Separation from Fats.—The mixture is saponified with caustic soda, and the saponified mass after cooling is exhausted with ether. On evaporating the ethereal solution, the cholesterol remains behind (Commaillie, *Compt. rend.* lxxxii, 819).

Isocholesterin (E. Schulze, *J. pr. Chem.* [2], vii, 163). This substance, isomeric with cholesterol, is obtained, together with the latter, by saponifying the grease of sheep's wool (*suint*) with alcoholic potash, and is deposited on cooling from a hot alcoholic solution, together with cholesterol, in white flocks (2nd *Suppl.* 328). To separate the isomeric alcohols, they are converted into benzoates, which, when treated with alcohol and crystallised from ether, yield shining rectangular leaflets and fine needles. These two kinds of crystals may be separated by elutriation and crystallised from ether; the shining leaflets are then found to consist of cholesteryl benzoate, and the needles of isocholesteryl benzoate. The latter digested with alcoholic potash yield ischolesterin.

Isocholesterin separates from absolute alcohol in flocks when the solution is dilute, but a concentrated alcoholic solution solidifies to a translucent jelly. When evaporated with nitric acid and afterwards treated with ammonia, it gives the same reaction as cholesterol, but when treated with sulphuric acid and iron chloride, or sulphuric acid and chloroform, it does not react like cholesterol (2nd *Suppl.* 331). Isocholesterin, like cholesterol, is slightly soluble in cold alcohol, but easily soluble in hot alcohol or ether. Hot acetic acid dissolves it readily, and the solution on cooling deposits flocks of an unstable compound of ischolesterin and acetic acid, which loses its acetic acid on fusion. Isocholesterin melts at 137° – 138° , and solidifies, on cooling, to a brittle vitreous mass. A mixture of cholesterol and ischolesterin melts at a lower temperature than either separately; one such mixture melted at 194° . Isocholesteryl benzoate melts at 190° – 191° , is very slightly soluble in alcohol, more soluble in hot acetone, and still more easily soluble in ether, from which it separates in microscopic needles. Isocholesteryl acetate is obtained by digesting ischolesterin with acetyl chloride till the evolution of hydrochloric acid ceases, and then heating the mixture to 100° in a sealed tube. On removing the excess of acetyl chloride by evaporation, ischocholesteryl acetate is obtained as an amorphous substance, melting below 100° , and easily soluble in alcohol. Isochocholesteryl stearate is obtained by heating ischocholesterin with stearic acid to 200° . The product melts at 72° , and separates from ether in microscopic needles, which dissolve to a small extent in hot alcohol and separate from it in flakes.

Phosphorus pentachloride converts ischocholesterin into a yellow resinous mass, easily soluble in ether, slightly soluble in alcohol, and having the composition of ischocholesteryl chloride, $C^{26}H^{36}Cl$.

A third alcohol, less rich in carbon than cholesterol, appears also to be contained in the insoluble portion of sheep's-wool grease, but it has not yet been isolated.

The potassium salts, which occur in considerable quantity in the portion of the grease which is soluble in water, probably arise from the saponification of the cholesterol salts. This may perhaps account for the presence of free cholesterol (E. Schulze, *J. pr. Chem.* [2], vii, 163).

**CHOLESTALIN }
CHOLEVERDIN } see BILE-PIGMENTS.**

CHOLINE, $C^4H^{10}NO^2$ — $C^4H^9N(CH^3)OH$. The bases of this composition obtained (α) synthetically from ethene-chlorhydrin and trimethylamine, and (β) from brain-substance, poultry-eggs, and the testicles of the salmon (1st *Suppl.* 448), appear from comparison of their platino-chlorides to be perfectly identical. Choline hydrochloride dehydrated as completely as possible—or, better, the platino-chloride—and gently heated with very strong nitric acid, yields muscarine (2nd *Suppl.* 823), the sparingly soluble platino-chloride of which is easily separated from undecomposed choline salt. With dilute nitric acid, no muscarine is obtained, but instead of it a nitro-product, which forms a very efflorescent platino-chloride, $(C^4H^9N^+O^2Cl)^2.PtCl_4 + 2H_2O$. Potassium permanganate and chromic acid sometimes convert choline partially into muscarine; sometimes not; betaine has never been found as a product of this reaction (Schmidberg u. Harmsack, *Chem. Centr.* 1876, 564).

Amanitine, an alkaloid occurring, together with muscarine (2nd Suppl. 829), in the fly-agaric, is likewise identical with choline; its gold-salt has the composition $C^4H^{14}NOClAuCl^2$. The separation of the two bases is effected by placing the mixture of their hydrochlorides on paper, which absorbs the more deliquescent muscarine salt, leaving the amanitine salt behind. A repetition of this process yields the latter pure; the muscarine may be separated in the form of aurochloride, which is more soluble than that of amanitine. Amanitine, like choline from other sources, gives off, when heated, trimethylamine and a volatile oxygenated base, together with other products (Harnack, *Chem. Centr.* 1876, 560).

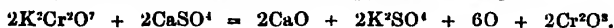
CHOLOGLYCOLLIC ACID, $C^2H^{12}O^7$, is produced by the action of nitrous acid on glycocholic acid. Its *barium salt* $(C^2H^{10}O^7)^2Ba + 3H^2O$, and *silver salt*, $C^2H^{10}O^7Ag$, have been prepared (J. Lang, *Bull. Soc. Chim.* [2], xxv. 180).

CHONDRIN. See GELATIN.

CHONDRODITE. See HUMITE.

CHONDROS. Various statements have been made regarding the presence of sulphur in the so-called *Irish pearl* or *Caragheen moss* (*Chondrus crispus*). According to Church (*Journal of Botany*, March 1876) it contains a large quantity of sulphur, only partly as sulphate. By oxidising the dried and pulverised alga with nitric acid and potassium chlorate, and precipitating the sulphuric acid with a barium salt, no less than 6.41 per cent. sulphur was obtained, while the ash contained only 2.64 per cent., 100 pts. of the fresh alga yielded 18.8 per cent. water, 9.38 albuminous matter, 55.54 gelatinous matter, &c., 2.15 cellulose and 14.15 ash.

When one part of potassium dichromate is heated with three parts of gypsum, the following reaction appears to take place:



On boiling the ignited mass with water or, better, with dilute hydrochloric acid, a fine powder of a rich green colour is obtained, having great tinctorial powers. It is very stable, resisting the action of water, acids, air, and sunlight (Casali, *Gazz. chim. ital.* iv. 664).

The pigment called *Plessy's Chrome-green* is prepared by adding calcium phosphate to potassium dichromate, and treating the mixture with sugar. It is not a definite compound, but a mixture of the phosphates of chromium, calcium, and potassium with chromic oxide and water (G. Köthe, *Dingl. pol. J.* ccxiv. 59).

CHROME-YELLOW. See CHROMATES (p. 461).

CHROMIUM. *Occurrence.*—Chrome-ores, which have been abundantly worked since 1858, occur in the serpentine of a triangular tract of land situated between Austria, Wallachia, and Servia. The principal ore is a coarsely crystalline chrome-iron ore, having a deep black colour, fatty lustre, and brown streak. Finely crystalline chrome-iron ore likewise occurs in clefts, with coatings of serpentine or chrome-ochre, and having rather a metallic than a fatty lustre.

The first three of the following analyses are of Hungarian chrome-iron ores, and show the varying amount of chromic oxide. Manganous oxide and lime are sometimes present, sometimes absent. This variety of constitution is remarkable, inasmuch as all the ores are from the locality above mentioned. No. 4 is an Asiatic chrome-iron ore (locality not further specified) given for the sake of comparison.

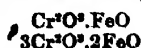
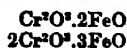
	1.	2.	3.	4.
Chromic oxide	58.096	17.096	39.574	60.022
Alumina	14.496	16.110	20.626	10.601
Ferric oxide	21.337	22.499	16.558	20.192
Magnesia	2.018	21.101	17.065	3.130
Manganous oxide . . .	0.002	—	—	5.200
Lime	—	8.300	—	0.026
Silica	3.639	14.211	4.190	—
	99.588	99.317	98.013	99.171

(A. Hoffmann, *Jahrb. f. Min.* 1873, 873).

Rich deposits of chrome-iron ore, frequently containing from 24 to 48 per cent. chromic oxide, are found in the serpentine rocks of the islands of Eubœa, Sinos, and Paros; in the Peloponnesus near Corinth; and in Phthiotis (Landerer, *Chem. Centr.* 1876, 590).

Christomanos (*Deut. Chem. Ges. Ber.* x. 343) gives the results of the analyses of

fifty specimens of chrome-iron ore from various localities in Greece and Asia Minor. These ores may be referred to four types represented by the formulæ:



On the occurrence of chrome-iron ore in the serpentine of Roarras and other localities in Norway, see Helland (*Jahrb. f. Min.* 1876, 670; *Chem. Soc. J.* 1877, ii. 120).

Estimation of Chromium in Chrome-iron ore.—F. C. Phillips (*Zeitschr. anal. Chem.* 1873, 189) decomposes the ore by heating it in a sealed tube with sulphuric acid of sp. gr. 1.34; mixes the resulting solution with excess of sodium carbonate; and adds bromine-water, with agitation. In this manner the chromium is obtained in solution as sodium chromate.

Dittmar (*Dingl. pol. J.* cexxi. 450) disintegrates chrome ores by melting them with a flux prepared by fusing 2 pts. of borax glass with 3 pts. of a mixture of sodium and potassium carbonates in equivalent proportion, till all the carbonic acid is expelled. The melt is dissolved in water, and the solution is boiled with a few drops of alcohol to reduce any manganates that may be present. The solution contains an alkaline chromate, the chromium in which may be estimated by any of the usual methods.

According to R. Kayser (*Zeitschr. anal. Chem.* 1876, 187), chrome-iron ore may be easily disintegrated by heating the finely levigated powder with 2 pts. of calcined sodium carbonate and 3 pts. of slaked lime.

The following volumetric method of estimation is described by Jean a. Pellet (*Bull. Soc. Chim.* [2], xxvii. 200). The fused mass obtained by heating the finely divided ore with alkaline carbonate is exhausted by boiling with water; the ferric oxide filtered off; the filtrate concentrated to about 400 c.c.; hydrochloric acid carefully added until there is only a slight alkaline reaction; and the whole refiltered (if necessary) and diluted to 500 c.c. Of this solution 250 c.c. are exactly neutralised with a few drops of dilute hydrochloric acid, and 50 c.c. of pure baryta-water added, then some carbonic acid water, and the whole boiled for a quarter of an hour in order to expel the excess of carbonic acid. When the solution is cold; it is diluted with water until it again measures 500 c.c., and 250 c.c. of the clear filtrate titrated with a standard sulphuric acid containing 12.58 grams of H_2SO_4 . 100 c.c. of this solution are equivalent to 0.25 gram. $\text{CrO}^{\text{O}}\text{K}^{\text{O}}$, and the number of cubic centimeters used corresponds exactly with the percentage of potassium chromate $\text{CrO}^{\text{O}}\text{K}^{\text{O}}$, which the chrome-iron ore would furnish.

The following precautions must be taken:

1. The sodium carbonate and hydrochloric acid used must be free from sulphuric acid, phosphoric acid, and calcium salts.
2. If a turbidity be observed on the addition of the standard sulphuric acid, the assay must be recommenced, as the carbonate of barium has not been completely precipitated, on account of insufficient boiling.
3. The baryta-water must be free from potash or soda, or at all events the amounts of these alkalis present must be accurately determined and deducted from the total alkali found.

The above process is applicable also to the assay of insoluble chromates which are decomposed by fusion with alkaline carbonates.

On the Estimation of Chromium in Iron and Steel.—See IRON.

Separation from other metals.—Gibbs recommends the use of bromine or chlorine to separate chromic oxide from the oxides of the third and fourth groups, in alkaline solution, or in presence of sodium acetate. Phillips (*Zeitschr. anal. Chem.* 1873, 189) finds that the separation of chromium from zinc, manganese, iron, and aluminium by means of bromine is complete. Traces of manganic acid and ferric acid may be decomposed by alcohol.

The presence of alumina hinders the reaction to some extent, and if alumina is present, the solution should be very dilute and should contain only a small excess of sodium carbonate. The solution must not be heated till after the addition of the bromine, for if water be added to the hot liquid, only small quantities of chromic oxide are converted into chromate, even after long heating.

Separation of Chromium from Uranium.—If the chromium exists in the mixture as chromate, together with only small quantities of chlorides or sulphates, and no acid is present, which, like phosphoric acid, can form a mercury salt not easily volatilised, the chromium may be precipitated by Berzelius's method, with mercurous nitrate. This salt must be free from nitrite, otherwise the chromic acid will be more or less reduced. The precipitation is best effected at the boiling heat, and the precipi-

pitate washed with a hot dilute solution of the nitrate. Precipitation with barium acetate, with addition of alcohol, also gives good results. Lead acetate gives a precipitate which passes through the paper. When chlorides or sulphates are present in large quantities, the solution may be boiled with soda. The sodium uranate is filtered off, washed with water containing soda, redissolved in hydrochloric acid, and the uranium determined as usual. The chromium in the filtrate may be precipitated by ammonia after reduction, for which purpose an alkaline nitrite is preferable to alcohol, since the time occupied in boiling off the latter is saved. When the chromium is not present as chromate, it must be converted into sodium chromate by boiling with a slight excess of soda and then adding bromine-water. The small quantity of chromium which, in this process, is precipitated with the sodium uranate formed in the reaction, is separated as above described (W. Gibbs, *Chem. News*, xxviii. 63).

Separation from Uranium and Iron.—The following method is an extension of that given by Deville (iii. 387) for the separation of iron and aluminium.

The mixture of the sesquioxides of the three metals, obtained by precipitation with ammonia, is weighed, after washing and ignition, in a porcelain boat, which is introduced in a porcelain tube and heated to redness in a current of hydrogen, whereby a mixture of iron, uranous oxide, and chromic oxide is obtained. The iron is removed from this mixture by passing over it, whilst heated to redness, a current of hydrochloric acid gas. After cooling in a stream of hydrogen, the mixture of uranous oxide and chromic oxide is weighed. The uranous oxide is then dissolved out by nitric acid, leaving chromic oxide, which is washed, ignited, and weighed. The difference between these two weighings gives the uranous oxide, which is calculated to U^2O^4 , and added to the weight of chromic oxide found. The sum of these deducted from the weight of the original mixture gives the weight of ferric oxide. The iron may also be determined directly by passing a current of steam mixed with a little hydrochloric acid through the tube after the removal of the boat. The chloride thereby formed is carried along by the water which condenses, and in this liquor the iron may be estimated by the usual methods. The uranium may also be estimated directly in the nitric acid solution. By this method iron and chromium can be separated, as also iron and uranium, and uranium and chromium (A. Ditte, *Ann. Chim. Phys.* [5], xii. 136).

OXIDES AND SALTS. Chromic Compounds. According to Kämmerer (*Zeitschr. anal. Chem.* 1873, 375), both chromic hydrate and chromic phosphate are soluble in alkalis, but on boiling the alkaline solution, only the hydrate is precipitated, so that phosphoric acid, if present, will be found in the filtrate.

Chromic Arsenite, $Cr^2As^2O^6$, is formed on mixing a hot concentrated solution of pure chromic acid with a hot saturated solution of arsenious acid. The liquid turns green and remains transparent; but if kept for some time at the boiling heat, it becomes turbid, and deposits the chromic arsenite in the form of a dark-green powder (R. Neville, *Chem. News*, xxxiv. 220).

Chromic Sulphates.—The salt $Cr^2(SO^4)^3 + 15H^2O$ was obtained some years ago in violet octohedrons by Schrötter and by Loewel (v. 588). Another violet salt, containing a larger quantity of water, is produced by dissolving 100 pts. of chromic anhydride in 150 pts. sulphuric acid and 225 pts. water, and acting on the solution with vapour of ether. By this means a salt is obtained which crystallises in plates permanent in the air; has at ordinary temperatures the composition $Cr^2(SO^4)^3 + 18H^2O$, analogous to that of crystallised aluminium sulphate; gives off 30.5 per cent. of its water at 100° ; and is converted, by loss of $12H^2O$, into a green crystalline sulphate, $Cr^2(SO^4)^3 + 6H^2O$, which is deliquescent, and convertible into the anhydrous salt at a dull red heat. The violet sulphate also loses part of its water, and is converted into the green sulphate, by leaving it in the state of fine powder, in contact with dehydrating liquids, such as fuming nitric or sulphuric acid, or phosphorus trichloride. The violet phosphate with $12H^2O$ is likewise converted into the green phosphate with $5H^2O$, by heating it to 100° , and behaves similarly to the violet sulphate with fuming nitric and sulphuric acids (Etard, *Compt. rend.* lxxxiv. 1089).

Double Chromic Sulphates belonging to the green modification, and represented by the general formula $Cr^mR^2(SO^4)^3$ or $Cr^2(SO^4)^3 \cdot 3R^2SO^4$, analogous therefore to the rhodic double salts, $Rh^mR^2(SO^4)^3$, and to the characteristic double salts of the cerium and yttrium groups, are produced: *a.* By adding chromic oxide or chromic sulphate, or a double salt $Cr^mR^2(SO^4)^3$ (obtained by heating an alkaline chromate with strong sulphuric acid), to the molten anhydrous bisulphates (pyrosulphates) of the alkali-metals, the mixture being kept in the fused state for eight to ten hours. On leaving the crucible to cool slowly, the melt solidifies to small green crystalline masses (Wernicke, *Pogg. Ann.* cliv. 572). *B.* By gradually adding chromic chloride

to a molten acid sulphate of alkali-metal, and extracting the excess of the latter with water, the chromic double sulphate then remaining undissolved :



(Etard, *Compt. rend.*, lxxxiv. 1089).

The *potassium salt* crystallises in greenish-yellow furry needles (Etard); in slender needles, which under the microscope appear prismatic with hexagonal outline, and therefore probably belong to the hexagonal system—a view which likewise agrees with their optical characters (Wernicke). The *sodium salt* is a crystalline powder (Etard); forms large crystals (Wernicke). The *lithium salt* forms slender needles, having a greyish-green colour with a tinge of violet-red (Wernicke).

All these salts are anhydrous, and are formed at comparatively high temperatures, whereas the formation of crystals of violet chromic salts appears to require a lower temperature and the addition of water. The green double sulphates above described assume a transient violet colour when gently heated, and on prolonged exposure to a red heat, they give off half their SO_3 , the remainder of the salt being resolved into Cr_2O_3 and 3RHSO_4 ; they are decomposed by boiling with potash, with separation of chromic hydroxide, and are easily broken up by fusion with nitre. They are insoluble in acids, whether dilute or concentrated, but appear to be decomposed by prolonged treatment with strong hydrochloric acid (Wernicke).

Dioxide or Chromic Chromate, $\text{CrO}_2 = \text{Cr}(\text{CrO}_2)\text{O}^+$. According to Hintz (*Liebig's Annalen*, clxix. 367), this oxide is best prepared by the method of Schweitzer (*J. pr. Chem.* xxxix. 269), which consists in passing nitrogen dioxide into a moderately dilute solution of potassium dichromate. The precipitate, which is formed more quickly on heating, consists of brown hydrated chromium dioxide, which must be washed, first with water, then with alcohol, and dried by prolonged heating at 250° . It gives off its water very slowly, a portion weighing only a few grams requiring a week to dry it. According to Schiff (*Liebig's Annalen*, clxxi. 116), the dioxide is best prepared by evaporating a mixture of potassium dichromate and oxalic acid with nitric acid.

Anhydrous chromium dioxide is a very hygroscopic powder having a fine deep black colour; the hydrate has a dark brown colour which was attributed by Vauquelin to the anhydride. It gives off oxygen at 300° . Dry chlorine acts but slightly on the black dioxide, even at 250° , forming a small quantity of chromatochloride or chlorochromate of chromium, $\text{Cr}^+\text{O}^+\text{Cl}^-$ (1st *Suppl.* 456), chromyl dichloride, CrO_2Cl_2 , being probably formed in the first instance, and converted at a higher temperature into the chromatochloride. The hydrated dioxide is also but very slightly attacked by chlorine, acquiring at the same time a dark colour. With dry gaseous hydrochloric acid, the anhydrous dioxide yields at first water, chlorine and green chromic oxide, then a small quantity of violet chromic chloride resulting from decomposition of the latter. Phosphorus pentachloride is likewise almost without action on chromium dioxide (Hintz).

Trioxide or Chromic Anhydride, CrO_3 . According to Ficinus (*Arch. Pharm.* [3], ii. 23; iii. 305), Warrington's method of preparing this oxide (which consists in mixing 1 vol. of a cold saturated solution of potassium dichromate with $1\frac{1}{2}$ vol. of strong sulphuric acid) often fails, in consequence of the acid employed not being strong enough, in which case no separation of the trioxide takes place. The addition of more sulphuric acid throws down only a small quantity of trioxide in red flocks. It is better, therefore, to evaporate the liquid over the water-bath till a small portion placed on a watch-glass crystallises on cooling, and then to allow the whole to stand for two days, whereby fine crystals are obtained.

When the trioxide is to be prepared frequently, it is advisable to use the residual sulphuric acid from a previous operation: it is then only necessary to evaporate somewhat longer over the water-bath. On using the same acid a third time, a little potassium bisulphate crystallises out with the chromic trioxide.

For preparing chromic trioxide once only, 1 part of a cold saturated solution of potassium dichromate may be mixed with 1 part of strong sulphuric acid, and the mixture evaporated over the water-bath. In this way a considerable saving of sulphuric acid is effected, whilst the product is as abundant, and as well crystallised as that obtained by Warrington's method.

Preparation from Barium Chromate.—By the following method the whole of the chromic trioxide contained in barium chromate may be quickly and easily obtained. 100 pts. of barium chromate are mixed with 100 pts. of water, and to this mixture 140 pts. of nitric acid of 40° strength of Baumé's hydrometer are added. The order of making the mixture is important. The liquid having been heated till it turns

red, 200 pts. of water are added, and the mixture is boiled for ten minutes. After that the solution is allowed to cool, whereupon barium nitrate is rapidly thrown down. The liquor, after decantation, is concentrated till its volume becomes about equal to that of the acid used. During this operation nearly all the barium that remains intact is deposited, not more than 0.5 pt. of the salt per 100 pts. of chromic trioxide being left. Finally, the excess of the nitric acid used is driven off by evaporating nearly to dryness, adding a little water, evaporating again, and so on several times, till no fumes are observable on testing with a rod wetted with ammonia. The chromic trioxide may then be easily crystallised out. It is very nearly pure, and may easily be obtained perfectly pure by precipitating the small trace of barium present with sulphuric acid, evaporating, and crystallising out the chromic trioxide.

The process here described might be carried out on a large scale. In that case the excess of nitric acid might be condensed, and the barium nitrate formed in the process might be employed for the making of barium chromate (Duvilliers, *Compt. rend.* lxxv. 211).

Reaction with Iodine.—When iodine is placed in a concentrated solution of chromium trioxide, the liquid becomes dark-coloured, and assumes a syrupy consistence. It refuses to crystallise, and may be rendered scaly by spreading on glass plates. When ignited it leaves a residue of green chromic oxide.

There appears to be some indication of the formation of a volatile compound of chromium and iodine, but if so, it is decomposed at a temperature but little above that at which it is formed, and it has not been isolated.

If to the solution of chromium trioxide and iodine, sulphuric acid be added, the iodine is rapidly oxidised to iodic acid; but the reduction of the chromic acid is never complete (J. Walz, *Chem. News*, xxvi. 245).

Combination of Chromic acid with Wool and Silk.—Chromic acid, notwithstanding its energetic oxidising power, possesses the property of uniting directly with wool and silk, and of producing with these animal fibres, without altering them, a yellow combination which will bear washing. To dye white wool, it is first passed through a bath at 60° containing sodium carbonate to the extent of about one-fifth the weight of wool, to get rid of the last traces of sulphurous acid, and then, after being washed, introduced into a bath of chromic acid composed, for each kilogram of wool to be dyed, of—

Potassium dichromate	60 grams
Sulphuric acid of 66°	50 "
Water	40 to 50 litres

To obtain a very fine straw-yellow, the wool is kept in the bath for some minutes at 30°; to obtain darker shades the skeins are turned for 20 minutes at a higher temperature, which, however, it is useless to raise above 60°. The wool is then washed in abundance of water.

As cotton is not dyed under these conditions, it may thus readily be detected when mixed with wool or silk.

The chromic acid combined with the wool retains some of its characteristic properties. Without leaving the animal fibre, it may be converted into lead chromate, or reduced by sulphurous acid to the state of oxide.

A variety of colours may be produced by further dyeing the yellow wool with logwood, madder, Brazil wood, &c.

When wool so dyed with chromic acid is introduced into a natural wine, it takes, after prolonged ebullition, a characteristic clear brown tint, always the same, wherever the wine has been produced. Such wool, placed in a mixture of wine and water fraudulently coloured, takes, if the added colour is influenced by chromic acid, a tint which shows clearly the nature of the fraud (Jacquemin, *Compt. rend.* lxxix. 523).

Chromates. Neutral potassium chromate, K_2CrO_4 , is converted into the dichromate $K_2CrO_4 \cdot CrO_3$ by the action of carbonic acid; also, with evolution of ammonia, when its aqueous solution is boiled with sal-ammoniac (F. Mohr, *Zeitschr. anal. Chem.* 1872, 278).

A salt which has the composition $K^2H^2Cr^2O^{11}$, and may perhaps be regarded as potassio-chromic dichromate, $\left\{ \begin{matrix} K^2O \\ (CrO_3)^2 \end{matrix} \right\} (CrO_3)^2 + H^2O$, is formed by the action of nitrogen tetroxide on a boiling solution of potassium dichromate in fuming nitric acid. It is a brown-violet amorphous powder, without taste or smell, insoluble in water, alcohol, acetic acid, &c. sp. gr. 2.28 at 14°. When heated above 300° it melts and decomposes, leaving a residue containing chromic oxide and potassium dichromate.

Nitric acid scarcely acts upon it at ordinary temperatures, but dissolves it partially, when heated, with formation of chromic acid. Sulphuric acid also does not dissolve it in the cold, but when heated with it, forms a solution, which, when neutralised with ammonia, yields ammonium chromate. Aqueous sulphurous acid dissolves it but slightly; hot concentrated hydrochloric acid dissolves it, with evolution of chlorine. A mixture of this salt with potassium chlorate detonates by heat, but not by percussion (Tommasi, *Bull. Soc. Chim.* [2], xvii. 396).

Potassium Chlorochromate, $\text{KCl} \cdot \text{CrO}_3$, treated with ammonia, yields, according to Heintze (2nd Suppl. 333), the salt $(\text{CrO}_3)_2(\text{OK})^2$. A. Leist, on the other hand, obtains by this reaction nothing but potassium dichromate mixed with ammonium dichromate and a small quantity of chromic oxide (*J. pr. Chem.* [2], v. 332).

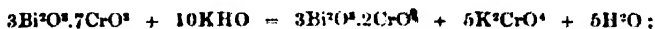
Lead Chromate.—When neutral lead chromate is treated with about twice its weight of boiling concentrated nitric acid, about 98.79 per cent. chromic acid and only 1.21 per cent. lead oxide are dissolved, the remainder of the lead being precipitated as nitrate in the crystalline form. On adding more water the whole of the lead is reconverted into neutral chromate, PbCrO_3 (Duvillier, *Ann. Chim. Phys.* [4], xxx. 204).

For the estimation of lead sulphate in commercial lead chromate (chrome-yellow, chrome-orange, &c.), Duvillier mixes 1 part of the pigment with 2 or 3 parts of nitric acid of 1.42 sp. gr., 1 to 2 parts of water and $\frac{1}{4}$ part alcohol, and gently heats the mixture. By careful evaporation to dryness, so as to avoid decomposition of the resulting chromic nitrate, and solution in water, the amount of undissolved lead sulphate may be determined with tolerable exactness (*Compt. rend.* lxxvi. 1362).

Wittstein (*Dingl. pol. J.* cxx. 280) regards this method as inexact, and recommends the following process for estimating the lead sulphate and other impurities present in chrome-yellow, such as the sulphates of barium and calcium, and carbonate of calcium. The pigment is boiled for half an hour with soda-solution, and the residue, after thorough washing, is dissolved in acetic acid; the liquid filtered from the undissolved barium sulphate is treated with hydrogen sulphide to precipitate the lead; the lead sulphide is dried at 100° and weighed; the barium still present is precipitated by sulphuric acid, and the calcium with ammonium oxalate. The alkaline liquid filtered from the lead, barium, and calcium precipitates is strongly supersaturated with hydrochloric acid, the sulphuric acid is precipitated by barium chloride, and then the chromic acid is thrown down by neutralising the acid with ammonia, adding a further quantity of barium chloride if necessary.

Bismuth Chromates.—Two of these salts were described by Löwe (i. 932), and four others have been prepared by Muir (*Chem. Soc. J.* 1876, ii. 15; 1877, i. 24, 646).

a. $3\text{Bi}^{2+} \cdot 2\text{CrO}_3$ is obtained by precipitating a nearly neutral solution of bismuth nitrate with potassium dichromate (Löwe), or by the action of caustic potash on the salt δ or ϵ (Muir). For its formation from the second of these salts Muir gives the equation:



its formation from δ may be represented by the equation:



Löwe describes it as an egg-yellow flocculent precipitate, which after a while becomes dense and crystalline. Muir obtained it in the form of a heavy dark brown-red salt, insoluble in water.

β . $\text{Bi}^{2+} \cdot \text{CrO}_3$, obtained by boiling the following salt with dilute nitric acid, or by treating it with alkali, is a vermillion-coloured salt, consisting of an aggregate of very minute microscopic needles, insoluble in water, but easily dissolved by dilute hydrochloric acid; it is also dissolved, though not so readily, by dilute nitric or sulphuric acid. Hot caustic soda-solution partly dissolves it, and partly converts it into a yellow chromate [probably $3\text{Bi}^{2+} \cdot 2\text{CrO}_3$].

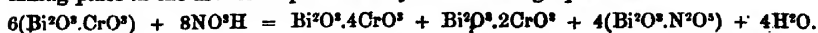
γ . $\text{Bi}^{2+} \cdot 2\text{CrO}_3$ is obtained by precipitating an acid solution of bismuth nitrate with potassium chromate, and crystallises with 1 mol. H_2O in orange-yellow needles, belonging, according to Burghardt's measurements, to the orthorhombic system, and apparently exhibiting the combination $\infty P \infty \cdot \infty P \cdot P$.

δ . $5\text{Bi}^{2+} \cdot 11\text{CrO}_3$, obtained by prolonged heating of γ with dilute nitric acid, is a heavy reddish-orange-coloured salt crystallising with $6\text{H}_2\text{O}$.

ϵ . $3\text{Bi}^{2+} \cdot 7\text{CrO}_3$ (at 100°), obtained by treating β first with strong and then with dilute nitric acid; is a light orange-coloured salt, insoluble in water, but easily dissolved by mineral acids, especially by hydrochloric acid. Strong hydrochloric acid dissolves it without the aid of heat, with evolution of chlorine and formation of a dark claret-coloured liquid. Cold caustic potash partly dissolves it, and converts it into a loose

bulky light yellow salt. Boiling potash converts it, and likewise the preceding salt, into the sesquibasic salt $3\text{Bi}^2\text{O}^3 \cdot 2\text{CrO}^3$.

$\text{Bi}^2\text{O}^3 \cdot 4\text{CrO}^3$ is obtained by boiling β with strong nitric acid, the reaction probably taking place in the manner represented by the following equation :



It forms red crystals, which appear under the microscope as monoclinic prisms, and contain 1 mol. H^2O , which is not given off at 100° . It is insoluble in water whether hot or cold, easily dissolved by dilute nitric or hydrochloric acid. Strong hydrochloric acid dissolves it, with evolution of chlorine. When very gently heated over a Bunsen flame, it parts with its water of crystallisation, and at high temperatures it decomposes, giving off red fumes, and leaving a dark green powder partly soluble in acids.

The mother-liquor of this salt, yields, when poured into water, a yellow precipitate, consisting of the salt $\text{Bi}^2\text{O}^3 \cdot 2\text{CrO}^3$, which is likewise obtained by dissolving the ruby-coloured salt in a small quantity of strong nitric acid and pouring the solution into water.

CHRYSAMMIC ACID, $\text{C}^{14}\text{H}^1\text{N}^1\text{O}^{12} = \text{C}^{14}\text{H}^1(\text{NO}^2)^4\text{O}^4$ (Liebermann & Giesel, *Deut. Chem. Ges. Ber.* viii. 1643; ix. 329). This acid, originally obtained from aloes by the action of nitric acid (i. 955), was formerly regarded as the tetranitro-derivative of chrysophanic acid, since De la Rue & Müller, by treating chrysophanic acid with fuming nitric acid, obtained a product which they regarded as identical with the chrysammic acid from aloes (*1st Suppl.* 460). Chrysophanic acid has however been lately shown by Liebermann & Fischer (*Deut. Chem. Ges. Ber.* viii. 1103) to be, not $\text{C}^{14}\text{H}^1\text{O}^4$, but $\text{C}^{14}\text{H}^{10}\text{O}^4$, that is to say a derivative, not of anthracene, $\text{C}^{14}\text{H}^{10}$, but of methylanthracene, $\text{C}^{14}\text{H}^{12}$. Hence if the tetranitro-derivative of chrysophanic acid is really identical with chrysammic acid from aloes (the analyses of which show that it contains only 14 atoms of carbon), the methyl-group of the chrysophanic acid must be removed by the oxidising action of the nitric acid going on simultaneously with the introduction of the NO^2 -groups.

To decide this question, Liebermann and Giesel have endeavoured to replace the nitril-groups of chrysammic acid from aloes by hydrogen, so as to obtain the non-nitrilised primary substance from which it is derived. If chrysammic acid is really tetranitrochrysophanic acid, the substance thus obtained should be chrysophanic acid; whereas if the product should be another substance reconvertible into chrysammic acid by direct nitration, then this substance, and not chrysophanic acid, must be the primary of chrysammic acid. The result has shown that chrysammic acid is a derivative, not of chrysophanic acid, but of anthracene, and has moreover brought to light the dioxyanthraquinone from which it is immediately produced.

Hydrochrysammide, $\text{C}^{14}\text{H}^{12}\text{N}^4\text{O}^4 = \text{C}^{14}\text{H}^1(\text{NH}^2)^4\text{O}^4$. This body, discovered by Schunck (*Ki.* 191), is the product of the action of reducing agents on chrysammic acid, and is formed from the latter by substitution of $(\text{NH}^2)^4$ for $(\text{NO}^2)^4$. When potassium chrysammate is added to a slightly alkaline solution of sodium sulphhydrate of sp. gr. 1.05, as long as it will dissolve (about 30 grains to a litre) reaction begins spontaneously, and may be assisted by heating the liquid for a short time to the boiling point. The blue solution must be quickly filtered and left to cool slowly, whereupon the whole solidifies to a mass of needles having a splendid coppery lustre. These are washed on a filter, first with water, then for several days with dilute acetic acid, to remove adhering inorganic salts, then dried, and exhausted with carbon sulphide to remove sulphur precipitated at the same time. The substance thus purified gave by analysis 55.26 to 55.83 per cent. carbon, 3.48 to 3.99 hydrogen, and 18.37 nitrogen, agreeing closely with the formula $\text{C}^{14}\text{H}^{12}\text{N}^4\text{O}^4$, which requires 56.00 per cent. C., 4.00 H., and 18.67 N., whereas the formula $\text{C}^{14}\text{H}^{12}\text{N}^4\text{O}^3$, proposed by Schunck, requires 50.60 C., 3.61 H., and 16.86 N.

Hydrochrysammide dissolves without alteration in strong sulphuric acid, and is reprecipitated therefrom by water. If only a small quantity of water be added, the whole solidifies to a pulp of yellow needles of a sulphate, from which the sulphuric acid is easily removed by a larger quantity of water.

Hydrochrysammide treated with nitrous acid is converted into a diazo-compound, and on boiling this compound with absolute alcohol, and pouring the alcoholic filtrate into water, a yellow precipitate is formed, consisting of chrysazin, $\text{C}^{14}\text{H}^1\text{O}^4$, one of the modifications of dioxyanthraquinone; and this substance, treated with fuming nitric acid, is converted into tetranitrochrysazin, $\text{C}^{14}\text{H}^1(\text{NO}^2)^4\text{O}^4$, identical in every respect with chrysammic acid obtained from aloes.

Respecting the crystalline form of chrysammic acid, and the properties of its salts, see p. 108 of this volume.

CHRYSAROBIN, *Araroba powder*, *Bakia powder*, *Goa powder*. These names are applied to the pith of a tree—belonging to the leguminous order, according to Dr

Silva (*Pharm. J. Trans.* [3], v. 723)—a species of *Cassalpinia*, according to Holmes (*ibid.*, 801), used as an external application in certain skin diseases. It is a very productive source of chrysophanic acid, containing, according to Attfield's analysis (*ibid.*, 721), 80–84 per cent. of that substance, together with 7 per cent. of arabin, bitter substances, and a glucoside (not further examined), 2 per cent. resinous matters, 5.5 woody fibre, 1 moisture, and 0.8 ash.

CHRYSEAN, $C^4H^4N^2S^2$ (Wallach, *Deut. Chem. Ges. Ber.* vii. 902). A sulphur derivative of hydrocyanic acid, formed by the action of hydrogen sulphide on a concentrated solution of potassium cyanide in water or in dilute aqueous ammonia. The best result is obtained by just covering 100–200 grams of potassium cyanide with water, and passing in sulphuretted hydrogen till the mass becomes black and opaque. The yellow flocks which settle to the bottom may then be separated by filtration, washed with cold water, and purified by crystallisation from hot water. The reaction may be represented by the equation:



Chrysean has a very beautiful colour, like that of mosaic gold. It dissolves with great difficulty in cold water, more easily in boiling water, and crystallises from the solution in flat, flexible needles: the aqueous solution has a neutral reaction. Chrysean is soluble also in alcohol and ether, as well as in acids and alkalis, and crystallises out unchanged. The solution in sulphuric acid or hydrochloric acid immediately imparts a red colour to pine wood.

In aqueous solutions of chrysean, *acetate of lead* produces, after a time, a dull white precipitate which soon turns black—the blackening takes place at once when heat is applied; *ferric chloride* with heat gives a black precipitate; *silver nitrate* a deep red precipitate, which very quickly becomes black; *platinic chloride* (with addition of HCl) produces at once a brown precipitate.

When the aqueous solution is warmed on the water-bath with *mercuric oxide* till the yellow liquid becomes colourless, and then filtered, a residue is obtained consisting of mercuric sulphide, and a filtrate containing basic mercuric cyanide, showing that the chrysean has been split up into sulphuretted hydrogen and prussic acid.

Nitrous acid produces a remarkable alteration in chrysean. If to an aqueous solution of chrysean some fuming nitric acid, or diluted nitric acid and zinc, or potassium nitrite and sulphuric acid, is added, the liquid is immediately coloured red, and the vessel becomes filled with red, spongy flocculi, which form when dry an amorphous mass having a green lustre. This red substance is very slightly soluble in water, but dissolves somewhat more easily, with fuchsine-red colour, in alcohol and ether. It is easily taken up by caustic soda and potash, also with a red colour, and is again thrown down on addition of acids. It is not, however, rendered pure by this operation, since partial decomposition takes place, as is evidenced by the smell of ammonia on solution in alkalis, and by that of sulphuretted hydrogen when it is precipitated by acids. The alcoholic solution of the red colouring matter shows very beautiful colour-reactions when mixed with alkalis. A fine, but very transient green colour is produced by the addition of very small quantities of an alkali; with larger quantities the solution is of a fine violet colour, but this soon passes into a dirty red.

CHRYSENE, $C^{14}H^{12}$. This hydrocarbon, originally found by Laurent among the last products of the distillation of coal-tar, is also produced, according to Berthelot, together with several others, when benzene-vapour is passed through a red-hot tube (1st *Suppl.*, 459; 2nd *Suppl.*, 338). G. Schultz (*Deut. Chem. Ges. Ber.* vi. 415) has obtained by this latter process four hydrocarbons, viz., diphenylbenzene, $C^{14}H^{14}$, melting at 205° , and an isomeride which melts at 85° ; also two others which melt at 266° and 196° respectively, the latter forming a picrate. He regards Berthelot's chrysene as different from the chrysene obtained from coal-tar, and as identical with diphenylbenzene. Berthelot, on the other hand (*Bull. Soc. Chim.* [2], xxii. 437), maintains that his chrysene obtained by decomposition of benzene is shown by analysis to have the composition of triphenylene, $C^{18}H^{12}$; moreover, that it differs from Schultz's diphenylbenzene by its property of combining with picric acid. He regards Schultz's hydrocarbon as a hydride of chrysene.

Chrysene is also formed, together with diphenyl-anthracene, hydrocyanic acid, ammonia, ammonium cyanide, and free carbon, when *acobenzene* is passed through a red-hot tube (Claus a. Secker, *Deut. Chem. Ges. Ber.* viii. 37).

Chrysene has been further investigated by E. Schmidt (*J. pr. Chem.* [2], ix. 250, 270), with the following results:

Pure chrysene, $C^{14}H^{12}$, may be prepared by the action of tin and hydrochloric acid on the compound of chrysene and dinitro-anthraquinone produced by treating an alcoholic solution of commercial anthracene with nitric acid (p. 464). It crystallises

from benzene or glacial acetic acid in well-defined colourless plates, belonging, according to Hahn's measurements, to the orthorhombic system. Axial ratio, $a : b : c = 1 : 1.376 : 2.490$. Combination, $P : OP$, the latter face predominating so far that the crystals appear like plates. Angle $P : P$ on the front terminal edge $= 150.6^\circ$; on the side terminal edge, 79.5° ; on the lateral edges, 144° . Chrysene melts at 250° , sublimates below its melting point in shining laminae, and boils at a temperature considerably above 360° . It dissolves but very slightly in alcohol, ether, carbon sulphide, benzene and acetic acid at ordinary temperatures, much more readily, especially in the last two solvents, at the boiling heat. The solutions as well as the crystals exhibit a deep reddish-violet fluorescence.*

ADDITION-PRODUCTS. Chrysene does not take up *hydrogen*, either when its alcoholic solution is boiled with sodium-amalgam, or when it is heated to 200° with concentrated hydriodic acid and amorphous phosphorus.

Trinitrophenol-Chrysene, $C^{18}H^{12}.C^6H^3(NO_2)^3O$, is obtained in long red needles, by gradual evaporation of a mixture of the moderately concentrated solutions of chrysene and picric acid in benzene.

Dinitroanthraquinone-Chrysene, $C^{18}H^{12}.C^{14}H^8(NO_2)^2O^2$, is obtained by dissolving 40–50 grams of the greenish-yellow commercial anthracene melting at 207° – 208° in 5 litres of alcohol of 95 per cent., adding 30 grams of nitric acid of sp. gr. 1.4 to the filtered solution, and boiling the liquid in a flask connected with a reversed condenser. The fine red needles thus formed are the pure compound.† It melts with partial decomposition at 294° , is almost insoluble in alcohol, ether, carbon sulphide, benzene and chloroform, and dissolves sparingly in boiling glacial acetic acid.

Dinitroanthraquinone-chrysene is converted by fuming nitric acid into dinitro-anthraquinone and tetranitrochrysene, and hot concentrated sulphuric acid decomposes it into a sulphonic acid of chrysene, and a dinitro-anthraquinone identical with Fritzsche's reagent (1st Suppl. 181, and p. 99 of this volume). Treated with tin and hydrochloric acid it yields chrysene and reduction-products of dinitro-anthraquinone. It was formerly regarded by Bolley as mononitro-anthracene (p. 94).

SUBSTITUTION-PRODUCTS. **Tribromo-chrysene**, $C^{18}H^{10}Br^3$, is formed by the action of bromine on a solution of chrysene in carbon sulphide. It is very sparingly soluble in all solvents, and crystallises from boiling benzene in well-defined glistening white needles, melting at 273° . When heated it sublimates in brilliant needles. Alcoholic potash acts on it only at 170° – 180° , chrysene being apparently regenerated. On boiling it carefully with potassium dichromate and sulphuric acid, or a solution of chromic trioxide in glacial acetic acid, chrysoquinone is formed. Fuming nitric acid dissolves it, with liberation of bromine and formation of nitro-products; the final product seems to be a tetranitro-chrysene.

Pulverised chrysene absorbs bromine-vapour, and is converted into a yellow-brown mass, from which, by washing with ether and recrystallisation from benzene, white needles are obtained, yielding by analysis 36.48 and 36.29 per cent. C., 1.64 and 1.49 H., 61.07 and 62.12 Br, whence they appear to consist of a mixture of tetrabromo-chrysene with more highly brominated derivatives.

Chlorochrysenes. When chlorine is acted upon by chrysene at 100° , the principal product consists of dichlorochrysene, $C^{18}H^{10}Cl^2$, which crystallises from benzene in soft white needles, melting at 267° . It is almost insoluble in alcohol, ether, and carbon sulphide, a little less soluble in hot benzene, and sublimates in brilliant needles. Alcoholic potash and nitric acid act on it under the same conditions as they do on the dibromo-compound. When chlorine is passed over chrysene at 160° – 170° , trichlorochrysene, $C^{18}H^8Cl^3$, is formed, which crystallises from benzene in fine needles, melting above 300° , and dissolving, but very sparingly, in boiling alcohol, ether, and chloroform.

Nitrochrysenes. Chrysene boiled with nitric acid in alcoholic solution is very slowly converted into mononitrochrysene, $C^{18}H^{11}(NO_2)$; the same compound is formed much more rapidly by heating the hydrocarbon with nitric acid of specific gravity 1.25 on a water-bath. It is purified by subliming the product and recrystallising the yellow needles thus obtained from benzene. ‡ It crystallises in thick prisms

* According to H. Morton (*American Chemist*, v. 115) the fluorescence and absorption spectra of chrysene, liquid or dissolved, are very much like those of anthracene, though not identical therewith. Solid chrysene exhibits 4, dissolved chrysene 5 maxima of light in its fluorescence spectrum, their positions being affected by the solvent (chloroform, benzene, turpentine-oil, ether). Two or three absorption-bands were observed. Insolation displaces the maxima of solid chrysene to the side of greatest refraction, and develops a fifth maximum.

† In the mother-liquor of this compound, different products are found, including anthraquinone and phenanthrene, which latter is not acted upon by nitric acid in an alcoholic solution, and is thus easily obtained pure.

which are grouped in stars, melt at 209° , and are very sparingly soluble in alcohol ether, and carbon sulphide, more freely in benzene and glacial acetic acid. When finely divided chrysene is boiled for some time with nitric acid of specific gravity 1.3, Laurent's *nitrite de chrysenase*, $C^{18}H^{10}O + N^2O^3$, is obtained, which is a mixture of the mono-, di-, and tetranitro-compounds. On heating this product carefully, the tetranitrochrysene is carbonised, while the two other compounds sublime. They are separated by recrystallisation from benzene or acetic acid. Dinitrochrysene, $C^{18}H^{10}(NO^2)^2$, is almost insoluble in alcohol, ether and benzene, and crystallises from glacial acetic acid in fine yellow needles melting above 300° ; it sublimes in long yellow needles. Tetranitrochrysene, $C^{18}H^4(NO^2)^4$, is formed from the preceding derivatives by the action of fuming nitric acid, or by prolonged boiling with very strong nitric acid. It crystallises in yellow needles, is nearly insoluble in all solvents, dissolves but sparingly in glacial acetic acid, melts at a temperature above 300° , and detonates at a stronger heat (Schmidt).

A yellow basic substance, said to be produced by boiling chrysene with water containing hydrochloric acid, and then adding ammonia (Phipson, *Chem. News*, xxx. 69).

W., $C^{18}H^4O^4$. This compound, the dioxiquinone of chrysene, has been extracted by Claus (*Deut. Chem. Ges. Ber.* viii. 157) from an artificial alizarin paste obtained from the factory of Meister, Lucius and Brünig. On neutralising this paste with potash, and subjecting the dried potassium-compounds to fractional boiling with alcohol, the chrysezarate is first dissolved, with blood-red colour, and afterwards the alizarate with violet colour. The two salts differ so greatly in their solubility in alcohol, that an almost quantitative separation may be effected in this manner. On evaporating the first alcoholic extracts, the chrysezarate remains as a neutral mass of dark-brown nearly black colour, quite different from the violet-brown of the alizarate.

Potassium chrysezarate dissolves readily in water, forming a yellow-red solution from which acids throw down the chrysezarin as a bulky gelatinous lemon-yellow precipitate.

Chrysezarin dissolves easily in boiling glacial acetic acid, and crystallises therefrom on cooling in dark brown needles having a splendid bronze metallic lustre; it dissolves readily also in alcohol and ether, remaining on evaporation of these solvents in the form of small yellow needles. It is insoluble in cold water, but dissolves sparingly in boiling water, forming a yellow solution, which on cooling deposits slender felted needles. It melts above 300° , and sublimes at 305° – 310° , mostly in feathery groups of broad needles having an orange-yellow colour and splendid lustre.

CHRYSYN, $C^{18}H^{10}O^4$ (J. Piccard, *Deut. Chem. Ges. Ber.* vi. 884; vii. 888). This substance, also called *chrysinic acid*, was first obtained by Piccard from the buds of *Populus nigra* and *P. pyramidalis*. He has since obtained it from the buds of *Populus monilifera* or *balsamifera*, and now adopts the following method of extraction: An alcoholic extract of 100 parts of the buds is precipitated by an alcoholic solution of 12 parts of lead acetate, and the next day the liquor is filtered from the precipitate, freed from lead by hydrogen sulphide, and subjected to distillation in order to remove the spirit. The acid liquor remaining in the retort deposits a resinous mass, which is to be once crystallised from spirit, and then freed from fat, rosin, sulphur, salicin, and populin, by successive treatment with absolute alcohol, ether, carbon sulphide, and boiling water. Boiling benzene now extracts from it a substance called *tecto-chrysin*. The impure substance is next fused at a temperature of 275° , in order to carbonize certain impurities, then dissolved in alcohol, and treated with a few drops of basic lead acetate, freed from lead by means of hydrogen sulphide, and finally crystallised twice from spirit.

Chrysin, when pure, forms bright yellow, thin, shining plates, which melt and sublime at 275° . It dissolves in about 60 parts of hot or 180 parts of cold alcohol. Acetic acid and aniline dissolve it with moderate facility, ether less readily, and carbon disulphide, petroleum, benzene, or chloroform scarcely at all. It is insoluble in water, but aqueous alkalis dissolve it with a yellow colour, and if the solution has not been long boiled, unaltered chrysin is precipitated on the addition of an acid; but by prolonged boiling with alkalis chrysin is resolved in phloroglucin, acetic and benzoic acids, and methyl-phenyl ketone. When an ammoniacal solution of chrysin is evaporated, unaltered chrysin remains, and the ammoniacal solution yields with calcium or barium chloride a yellow precipitate, which becomes black when exposed, in the moist state, to the air. An alcoholic solution of chrysin is precipitated by lead acetate, but the precipitate is soluble in excess of the reagent or in acetic acid. Ferric chloride strikes a violet colour with an alcoholic solution of chrysin. Concentrated

sulphuric acid and nitric acid dissolve it with a yellow colour, and the latter solution deposits granular crystals of nitrochrysin.

Dibromochrysin, $C^{12}H^8Br^2O^4$, is obtained by mixing an alcoholic solution of chrysin with excess of bromine, and washing the slender needles which are deposited, with alcohol containing bromine. When dried over sulphuric acid, it forms a felted mass of silky crystals which become exceedingly electric on pulverisation.

Diiodochrysin, $C^{12}H^8I^2O^4$.—When iodine is added to an alcoholic solution of chrysin, the action is slow and incomplete, but the addition of iodic acid causes it to take place rapidly, needles of diiodochrysin being deposited. The same compound is formed when a solution of iodine in potassium iodide is added to an alkaline solution of chrysin. Diiodochrysin is less stable than the bromine-compound, losing weight and changing colour at 100° .

Dichlorochrysin, $C^{12}H^8Cl^2O^4$, is obtained in needles when a solution of chrysin in acetic acid was subjected to the action of a stream of chlorine.

Dinitrochrysin, $C^{12}H^8(NO^2)^2O^4$.—A cold saturated solution of chrysin in strong nitric acid soon becomes warm, evolves nitrous fumes, and deposits a crystalline substance. The same body may be obtained by adding dilute nitric acid to chrysin, and evaporating off the acid. The product thus obtained is contaminated with oxalic acid, resinous substances, and aromatic oily substances. It is purified by being first boiled with water and then with alcohol, after which the residue is dissolved in ammonia, and on evaporating this solution, crystals of ammonium dinitrochrysin are obtained. This salt is easily purified by crystallisation, and may then be decomposed by an acid.

Dinitrochrysin is almost insoluble in alcohol, ether, benzene, &c., but dissolves in hot acetic acid or aniline, from which it may be obtained in large crystals. It forms two compounds with ammonia, an orange-red *basic salt* which is very slightly soluble, and is decomposed by being boiled with water into ammonia and the *acid salt*. This latter has a bright yellow colour, and does not lose all its ammonia when water is repeatedly evaporated from it.

Homologues of Chrysin, $C^{12}H^8(C^2H^{2n+1})O^4$, Piccard (*Deut. Chem. Ges. Ber.* vi. 891; vii. 894; x. 176). These bodies are formed by treating chrysin dissolved in methyl-, ethyl-, and amyl-alcohol with the corresponding iodides, $C^2H^{2n+1}I$, and boiling the products with potash. They are easily separated from unaltered chrysin by extraction with chloroform, which leaves the chrysin undissolved.

Methylchrysin, or *Tectochrysin*, $C^{14}H^{12}O^4 = C^{12}H^8(CH^3)^2O^4$, exists in poplar-buds, together with chrysin, is contained in the first crude product of the preparation of the latter, and may be separated therefrom by its much greater solubility in benzene. It is much less soluble in alcohol than chrysin, and crystallises from alcohol or from benzene in large, well-defined, sulphur-yellow, monoclinic prisms, exhibiting the three following combinations:

$$(1). 0P. \infty R \infty. \infty P. \frac{P}{2}.$$

$$(2). 0P. \infty R \infty. \infty P.$$

$$(3). 0P. \infty R \infty. \infty P2. \frac{P}{2}.$$

Axial ratio:	Principal axis:	Clinod.:	Orthod.
	1.54	1	1.86

Angle of inclined axes = 53.6° .

Methylchrysin melts at 163° – 164° . Its bromine-derivative has the composition $C^{14}H^{10}Br^2O^4$.

Ethylchrysin forms long, silky, thin needles melting at 146° .

Amylchrysin, from amylic alcohol of fermentation, likewise forms thin needles which melt at 125° .

Dibromamylchrysin, $C^{16}H^{12}Br^2(C^2H^5)^2O^4$, formed by evaporating a solution of bromine and amylchrysin in chloroform, crystallises in slender needles.

Methyl-, ethyl-, and amyl-chrysin all dissolve sparingly in alcohol, easily in benzene and carbon bisulphide, and with great facility in chloroform, and are thereby perfectly distinguished from chrysin.

Chrysin, as already observed, dissolves in alkalis with deep yellow colour, and is resolved by prolonged boiling therewith into phloroglucin, acetic and benzoic acids, and methylphenyl ketone, whereas the above-named derivatives are not soluble in alkalis and are but very slowly attacked by them. It follows, therefore, that chrysin is a phenol, of which the methyl and other derivatives are ethers, and that chrysin contains only one hydroxyl-group.

CHRYSOCOLLA. *Cupric silicate* (v. 252).—L. Hutchings, *Chem. News*, xxxiv. 141, xxxvi. 18. This mineral occurs in large quantities, together with copper pitchblende (*Kupferpecherz*) in Mexico, and both these minerals are imported into England for copper-smelting. The chrysocolla is light bluish-green: hardness = 4.0; the copper-pitchblende dark brown, almost black: hardness = 6.0. It contains large quantities of gypsum intermixed, and here and there copper carbonates. When large lumps are broken open, they often show drusy cavities in which the chrysocolla occurs in botryoidal forms. This botryoidal chrysocolla is always coated with a thin layer of quartz, sometimes amorphous, but more frequently in very minute crystals. The minerals, which were very pure, were dried at 85° for some hours previous to analysis:

	Chrysocolla.	Copper-pitchblende.
Silica soluble in Na_2CO_3	62.42	20.63
Silica insoluble in Na_2CO_3	3.83	7.35
Copper oxide	26.69	28.59
Lead oxide	0.12	0.41
Ferric oxide	0.26	10.94
Alumina	—	0.15
Manganous oxide	trace	17.53
Oxygen	—	3.6
Cobalt oxide	trace	0.35
Zinc oxide	0.34	1.54
Lime	0.74	0.92
Magnesia	1.06	—
Water	6.13	8.30
	100.69	100.31

Chrysocolla likewise occurs in Lower California, in two distinct varieties, one portion of a lump being hard, vitreous, and of a fine bluish colour, while another portion is soft, earthy, pale bluish-white, and so light and porous as sometimes to float on water. One specimen was found to absorb 86.6 per cent. of its own weight of water.

The following are analyses of a vitreous and an earthy specimen, the finely pounded minerals having been dried at 95° for some hours:

	SiO_2 .	CuO .	PbO .	Fe_2O_3 .	Al_2O_3 .	ZnO .	CaO .	MgO .	H_2O .	
Vitreous	67.07	24.95	0.26	0.27	0.55	0.09	0.81	0.37	5.86	= 100.22.
Earthy	46.46	39.15	0.41	0.48	3.65	0.10	0.80	0.82	7.99	= 99.86.

The mineral of these deposits is doubtless true chrysocolla mixed with large quantities of opal silica, and containing a certain amount of silica very finely disseminated through the mass as quartz and chaledony. The proportion of this, roughly estimated, is about 3 per cent. in the vitreous and less than 1 per cent. in the earthy variety. The latter is more or less fusible, apparently in consequence of its larger proportion of alumina, while the vitreous mineral is not at all fusible.

The chrysocolla ore of Lower California likewise contains a small quantity of what appears to be another variety of copper-pitchblende. Its hardness is 2 to 3, streak black, and it melts easily before the blowpipe, differing in these respects from the variety above described. Its composition is:

SiO_2 .	CaO .	Fe_2O_3 .	FeO .	CuO .	MnO .	O .	CaO .	MgO .	SO_2 .	H_2O .
11.96	14.20	9.35	0.80	0.95	38.53	7.89	2.41	2.35	0.16	11.61 = 100.20.

It is found only in thin layers, alternating with chrysocolla and fibrous gypsum.

Aluminous Chrysocolla from Utah. Colour, light greenish-blue; streak pale-blue; subtranslucent; hardness not much over 2.

SiO_2 .	Al_2O_3 .	CuO .	H_2O .
37.19	10.78	26.03	25.76 = 99.76.

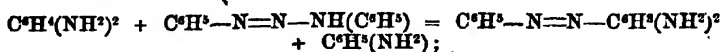
Hence the formula, $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$, one half the copper being replaced by an equivalent amount of aluminium (Santon, *Chem. News*, xxxvi. 167).

CHRYSOIDINE or I

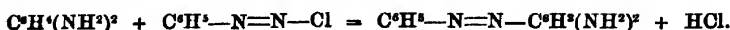


(O. N. Witt, *Deut. Chem. Ges. Ber.* x. 350, 654; A. W. Hofmann, *ibid.* 326). This base, intermediate in composition between monamidazobenzene, $\text{C}^6\text{H}^3\text{N}^4 \cdot \text{NH}^2$ (aniline-
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yellow), and triamidazobenzene, $\text{C}^6\text{H}^3\text{N}^2(\text{NH}^2)^3$ (phenylene-brown), was first observed by Caro (December, 1875), who obtained it by the action of metadiamidobenzene (*m*-phenylenediamine) on diazo-amidobenzene:



and some of its salts were prepared soon afterwards (January 1876) by Witt (without previous knowledge of Caro's result), by the action of *m*-diamidobenzene on various salts of diazobenzene, *e.g.* the hydrochloride,



These salts form colouring matters of yellow or orange tint; the hydrochloride, known commercially as *chrysoïdine*, has a splendid orange-yellow colour.

To prepare chrysoïdine, a 1 per cent. solution of a diazobenzene salt is mixed with a 10 per cent. solution of metadiamidobenzene; * the resulting blood-red precipitate is dissolved in boiling water; the solution after cooling to 50° is precipitated with ammonia; and the precipitate is crystallised, first from alcohol of 30 per cent. and then from boiling water.

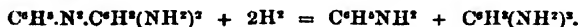
Pure chrysoïdine thus prepared forms slender needles of a fine yellow colour, only sparingly soluble in water even at a boiling heat, easily soluble in alcohol, ether, chloroform, benzene, and aniline. It melts at 117·5° (Witt); at 110° (Hofmann).

Chrysoïdine is a moderately strong base, but does not form stable salts with more than 1 mol. of acid. The *mono-acid salts* dissolve without decomposition in hot water, forming solutions of a splendid yellow colour; and on adding a large excess of acid, the *bi-acid salts* are produced, which have a fine crimson colour in solution, but cannot be obtained in the solid state. The mono-acid salts crystallise from their hot solutions in two different forms, which often occur together. By slow cooling, thick, highly lustrous black octohedrons are obtained, often grouped in steps; by rapid cooling, in presence of free acid, and with the use of certain solvents, long, shining, blood-red prisms are formed, mostly in fan-shaped or palmate groups. On very rapid cooling, the solution coagulates to a jelly formed of closely packed slender microscopic needles. In these respects the hydrochloride, nitrate, sulphate, and oxalate resemble one another very closely. The *acetate* is an uncrystallisable black syrup, soluble in all proportions of cold water.

The hydrochloride unites with metallic chlorides, forming well-crystallised double salts. The *zinc salt* is a brown-red crystalline precipitate, moderately soluble in cold water, insoluble in a solution of zinc chloride (Witt).

Chrysoïdine, as already mentioned, is intermediate in composition between aniline-yellow and phenylene-brown, these three dye-stuffs being members of a series all the terms of which contain the group $-\text{N}=\text{N}-$. It is also intermediate in tinctorial power. A given quantity of chrysoïdine will dye twice as much silk to a given depth of colour as the same quantity of aniline-yellow; and phenylene-brown in the pure state exhibits about three times the tinctorial power of aniline-yellow. In different dye-stuffs belonging to the same group, the tinctorial power increases with the salt-forming capacity, whereas the tone of colour varies to a certain extent with the molecular weight (Witt).

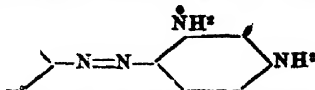
Reactions.—1. By the action of mild reducing agents, such as *zinc-dust* and *acetic acid*, chrysoïdine appears to be converted into hydrazo-compounds, light yellow solutions being formed which greedily absorb oxygen, with reproduction of chrysoïdine. With *tin* and *hydrochloric acid*, on the other hand, chrysoïdine is resolved into aniline and triamidobenzene:



The resulting solution having been freed from tin by hydrogen sulphide, from the latter by boiling, and rendered alkaline, yields when distilled a milky liquid separable by repeated distillation into aniline and a residual liquid which when exposed to the air or treated with oxidising agents, yields a red-brown colouring matter agreeing in all its characters with that which is obtained by oxidation of the triamidobenzene formed by reduction of (1 : 2 : 4) dinitraniline. Hence it follows that the triamidobenzene obtained, together with aniline, by reduction of chrysoïdine, has its three NH^2 -groups in the relative position 1 : 2 : 4, and consequently that in chrysoïdine itself the same relative positions must be occupied by the N^2 -group and the two NH^2 .

* Paradiamidobenzene similarly treated does not yield a trace of colouring matter: the behaviour

groups, that is to say that the constitution of chrysoidine must be represented by the formula



Diacetyl-chrysoidine (*infra*) submitted to the action of powerful reducing agents yields, with separation of the acetyl-groups, the same reduction-products as chrysoidine itself.

2. *Dry distillation*.—On heating chrysoidine or its acetate in a retort to 150° – 175° , or the hydrochloride to 200° , or chrysoidinesulphonic acid (*infra*) to 250° , or diacetylchrysoidine to above 300° , the mass fuses, swells up, blackens, and yields an oily distillate of aniline, leaving in the retort a very bulky, shining, carbonaceous mass, from which—if obtained from the hydrochloride—acidulated alcohol extracts a reddish-violet dye-stuff, apparently identical with chrysoidin-indulin (*infra*), and produced by the action of the aniline resulting from the decomposition, on the still undecomposed chrysoidine salt.

3. *Decomposition with addition of water*.—Chrysoidine heated with dilute hydrochloric acid to 150° – 160° in sealed tubes, undergoes a decomposition similar to that which takes place when diazobenzene-compounds are heated with water (e.g. $C^6H^5.N^2.NO^2 + H^2O = C^6H^5.OH + N^2 + NO^2H$), nitrogen escaping when the tube is opened, and a blackish liquid being formed, which, when largely diluted with water and distilled, yields a considerable quantity of phenol, while the residue in the retort forms a brown-red solution of a colouring matter apparently identical with that which is produced by oxidation of triamidobenzene.

4. *Action of Amides*.—Chrysoidine, like other amidazo-compounds, yields, with aromatic amides, new colouring matters belonging to the numerous group of the indulins (*q.v.*) As yet, however, only one has been prepared, viz., with aniline, which is a dingy violet body, apparently identical with that which is obtained from the residues of the dry distillation of chrysoidine hydrochloride.

5. *Action of Nitrous acid*.—Under certain circumstances chrysoidine appears to be convertible by nitrous acid into a diazo-compound, which, however, is so unstable, that it decomposes, even at ordinary temperatures, with evolution of nitrogen and separation of a black humus-like substance. A similar mode of decomposition is exhibited by the diazo-compound of metaphenylenediamine.

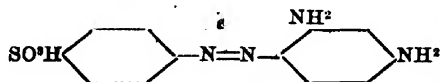
Substitution-derivatives. *Dimethyl-chrysoidine*, $C^{12}H^{10}(CH^3)_2N^4$, is formed, as a hydriodide, by heating chrysoidine with methyl iodide. The free base crystallises indistinctly from hot water containing a little alcohol. *Tetramethyl-chrysoidine*, $C^{14}H^{14}(CH^3)_4N^4$, formed by the action of diazobenzene-salts at ordinary temperatures on tetramethylphenylenediamine, appears to be uncrystallisable. *Dibenzylchrysoidine*, $C^{18}H^{18}(C^6H^5)_2N^4$, is formed by the action of benzyl chloride at 100° on chrysoidine. These three bodies dye silk and wool a fine yellow, with a tinge of red deeper as their molecular weight is higher; the last in particular is a dye-stuff with a splendid lustre.

Diacetylchrysoidine, $C^{12}H^{10}(C^2H^3O)_2N^4$, prepared by treating chrysoidine with excess of acetic anhydride, boiling the product with alcohol, and recrystallising it from boiling glacial acetic acid, crystallises in stellate groups of short thick prisms, or small needles having an orange-yellow colour and adamantine lustre, and exhibiting on certain faces a faint bluish dichroism.

Chrysoidinesulphonic acid, $C^{12}H^{11}N^4.SO^3H$, is formed by heating chrysoidine on the water-bath with strong sulphuric acid. On pouring the product into water, a bulky precipitate is formed; and on washing this with water, dissolving it in ammonia, and treating the boiling solution with barium chloride, the liquid on cooling yields crystals of barium chrysoidinesulphonate, which may be purified by recrystallisation. A solution of this salt mixed with the calculated quantity of hydrochloric acid, yields a dark-brown precipitate of chrysoidinesulphonic acid, which on boiling changes, without perceptibly dissolving, into a mass of crystals, which when washed and dried are red with a metallic lustre, and very much like amorphous phosphorus. They dissolve with moderate facility in dilute sulphuric acid, and with splendid carmine colour in strong hydrochloric acid.

Barium Chrysoidinesulphonate, $(C^{12}H^{11}N^4.SO^3)^2Ba$, forms anhydrous brown shining crystalline scales. The other salts may be formed from it by double decomposition. The *sodium-salt* is easily soluble, and crystallises in scales having the colour of mosaic gold, which also separate on drenching the free acid with strong soda-ley. The *cuprio salt* is quite insoluble, and separates by precipitation at ordinary temperatures as a brown-red substance, which becomes dark-red and crystalline on boiling. The *ferric*

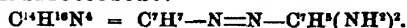
Chrysoidinesulphonic acid subjected to dry distillation yields small quantities of aniline, the greater portion of the mass being carbonised. It is not acted upon by acetic anhydride at 100°, or by aniline at the boiling heat. On reducing it with tin and hydrochloric acid, and distilling the product after freeing it from tin, &c., and rendering it slightly alkaline, scarcely a trace of aniline is obtained. Hence it may be inferred that the sulpho-group in this acid is attached to the benzene-ring which is the residue of the aniline group of chrysoidine—most probably in the para-position—so that the constitution of chrysoidinesulphonic acid will be represented by the formula



Chrysoidinesulphonic acid, like the base itself, produces fine colours, though somewhat tinged with brown; but its value as a dye-stuff is to a certain extent impaired by the fact that fabrics dyed with it are apt to change colour during the process of clearing.

Homologues of Chrysoidine. A considerable number of these bodies might be produced by the action of diazobenzene salts on tolylenediamine and its higher homologues, and further by subjecting these diamines to the action of salts of diazo-toluene, diazoxylene, &c. Only one has, however, yet been prepared, viz., by treating tolylenediamine (m. p. 99°) with a salt of the diazotoluene prepared from paratoluidine.

This base is diamidazotoluene:



Its colour is, if possible, finer than that of chrysoidine, and both the free base and its salts crystallise with greater facility than the latter. The base separated by aqueous ammonia from the boiling alcoholic solution of the hydrochloride crystallises on cooling in fine orange-yellow needles usually grouped in stars. It dissolves easily in alcohol and ether, but is almost insoluble in water, even at the boiling heat. It melts at 183° (Hofmann).

CHRY SOLIN. A yellow colouring matter produced by the action of phthalic anhydride on benzyl-resorcin. See RESORCIN

CHRY SOLITE. On the occurrence of this mineral in dolerite, see DOLERITE.

CHRY SOPHANIC ACID. This acid has hitherto been regarded as a derivative of anthracene, $\text{C}^{14}\text{H}^{10}\text{O}^4$ or $\text{C}^{14}\text{H}^{10}\text{O}^4$, inasmuch as it was supposed to yield anthracene when heated with zinc-dust (*2nd Suppl.* 340). It has, however, been lately shown by Liebermann a. Fischer (*Deut. Chem. Ges. Ber.* viii. 1102) that the hydrocarbon thus obtained is not anthracene, but methyl-anthracene, $\text{C}^{15}\text{H}^{12}$ (giving by analysis 93.88–93.92 per cent., and 5.82–6.23 H.; calc. 93.75 C., and 6.25 H., and convertible by oxidation with nitric acid into methylanthraquinone, $\text{C}^{15}\text{H}^{10}\text{O}^2$; anal. 80.8 C. and 4.6 H.; calc. 81.1 C., 4.6 H.).

Hence it may be inferred that chrysophanic acid is not dioxyanthraquinone, but dioxymethylanthraquinone, $\text{C}^{15}\text{H}^{10}\text{O}^4$, and this conclusion is confirmed by the analysis of chrysophanic acid and its diacetyl-derivative.

<i>Chrysophanic acid.</i>			
Analysis.			
Carbon .. .	70.87	70.29	Calc. $\text{C}^{15}\text{H}^{10}\text{O}^4$. 70.87
Hydrogen . . .	4.12	4.02	3.94
<i>Acetylchrysophanic acid.</i>			
Analysis.			
Carbon .. .	66.98		Calc. $\text{C}^{17}\text{H}^8(\text{C}^2\text{H}^3\text{O}^2)^2\text{O}^4$. 67.45
Hydrogen. . .	4.16		4.14

Chrysophanic acid may therefore be represented by the formula $\text{C}^{15}\text{H}^8 \left\{ \begin{smallmatrix} \text{CH}^3 \\ \text{O}^2 \end{smallmatrix} \right\}^2$, and

is related to emodin (g.v.) in the same manner as alizarin to purpurin. The two principal colouring-matters of rhubarb-root, chrysophanic acid, and emodin, are in fact derived from methyl-anthraquinone in the same manner as alizarin and purpurin, the two principal colouring-matters of madder-root, are derived from anthraquinone (Liebermann a. Fischer).

Tetranitrochrysophanic Acid, $\text{C}^{15}\text{H}^8(\text{NO}^2)^4\text{O}^4$. This acid was formerly supposed to be identical with chrysammic acid: but the recent experiments of Liebermann a. Giesel (*Deut. Chem. Ges. Ber.* viii. 1643: ix. 329) have shown that this is not

the case, and that chrysammic acid is the tetranitro-derivative, not of chrysophanic acid, but of chryszazin, $C^{12}H^4O^4$ (p. 108).

Potassium nitrochrysophanate, $C^{12}H^4(NO^2)_4O^4K^2$ (at 120°), forms jelly-like groups of thin red needles, very soluble in pure water, sparingly in saline solutions. The *calcium salt*, $C^{12}H^4(NO^2)_4O^4Ca$ (at 125°), forms indistinct jelly-like groups of thread-like needles, destitute of metallic lustre (the chrysammate is highly lustrous). The *magnesium salt*, $C^{12}H^4(NO^2)_4O^4Mg$ (at 160°), is a red sparingly soluble powder.

Amides of Chrysophanic Acid (Liebermann & Fischer, *Deut. Chem. Ges. Ber.* viii. 1105. 1. *Chrysophanamide*, or *Amidochrysophanic acid*, $C^{12}H^{11}NO^4$

or $C^{12}H^8 \begin{Bmatrix} OH^2 \\ NH^2 \\ OH \\ O \end{Bmatrix}$. When chrysophanic acid is heated to 200° with aqueous ammonia,

chrysophanamide is formed, together with carbonaceous products; at 150° , on the other hand, no carbonaceous products are formed, but the resulting chrysophanamide is accompanied by a substance which separates in long dark shining needles. The chrysophanamide is precipitated from the crude product by addition of an acid, dissolved in alcohol containing hydrochloric acid, precipitated by water, converted into barium salt, once more precipitated by an acid, and then crystallised from alcohol, which deposits it in yellow leaflets. It is decomposed by boiling baryta-water into ammonia and chrysophanic acid.

The crude product of the action of ammonia on chrysophanic acid contains also a compound of chrysophanamide and ammonia, $C^{12}H^{11}NO^2.NH^2$, which is not completely decomposed either by solution in baryta-water or by precipitation with hydrochloric acid. To obtain the amide quite pure, it is therefore necessary to digest the impure product with warm alcohol containing hydrochloric acid, whereby however it is partly resolved into ammonia and chrysophanic acid.

2. *Chrysophanimide*, $C^{12}H^8NO^2 = C^{12}H^8 \begin{Bmatrix} CH^2 \\ NH \\ O^2 \end{Bmatrix}$. The long dark shining needles

mentioned above as produced, together with chrysophanamide, when chrysophanic acid is heated with aqueous ammonia to 150° , consist of the ammonia-compound of this imide, $C^{12}H^8NO^2.NH^2$. It has not been found possible to obtain the free imide, because the ammonia-compound is converted by prolonged treatment with acids or alkalis into chrysophanic acid. But by heating this ammonia-compound with acetic anhydride in a vessel with reversed condenser, it is converted into acetylchrysophanimide

$C^{12}H^8 \begin{Bmatrix} CH^2 \\ N.C^2H^3O. \\ O^2 \end{Bmatrix}$. This substance in its external properties bears a close resemblance

to xylindrin. It separates from chloroform in violet needles, which have a metallic lustre, are but slightly soluble in the ordinary solvents, resist soda-solution, and dissolve in warm nitric or sulphuric acid, with reproduction of chrysophanic acid. An analogous substance is formed by the action of isobutyric anhydride on the ammonia-compound of chrysophanimide.

CHRYSOPHYLL. See LEAVES, COLOURING MATTERS OF.

CHRYSOQUINONE, $C^{12}H^{10}O^2$ (Graebe, *Deut. Chem. Ges. Ber.* vii. 782. E. Schmidt, *J. pr. Chem.* [2], ix. 250, 270) This compound, discovered by Liebermann, is obtained by the action of chromic acid on chrysene dissolved in acetic acid (2nd Suppl. 339). It crystallises, according to Schmidt, in brilliant red needles, melting at 235° , according to Liebermann at 220° . It unites with alkaline bisulphites, forming colourless compounds soluble in water. The sodium salt, probably $C^{12}H^{10} \begin{Bmatrix} OH \\ O.SO^2Na \end{Bmatrix}$, is most easily prepared by heating chrysoquinone, previously drenched with alcohol, with a solution of sodium bisulphite. The chrysoquinone then dissolves, and the concentrated solution deposits crystals of the sodium-compound, which are decomposed by water, with liberation of chrysoquinone. This is the best method of separating chrysoquinone from unaltered chrysene (Graebe).

In its behaviour to alkaline bisulphites, chrysoquinone resembles phenanthrenequinone, but differs from anthraquinone, which is not dissolved by alkaline bisulphites in presence of alkaline carbonates.

The analogy of chrysoquinone to phenanthrenequinone is likewise shown by its reaction with sulphurous acid, whereby it is converted into chrysohydroquinone, $C^{12}H^{12}(OH)^2$ (2nd Suppl. 340), the reaction taking place with the aqueous acid at 100° , and with the alcoholic acid even at ordinary temperatures, but more quickly when heated. Anthraquinone is not altered by sulphurous acid, even at temperatures above 200° .

The results of the analysis of number 14 lead to the conclusion that it cannot be a variety of *Cincho officinalis*. According to J. E. Howard it is probably *Cinchona erythraea*.

2. Barks of *Cinchona succirubra* and *C. pahudiana* cultivated at Oetacamund (de Vrij, *ibid.* 869).

100 pts. of the bark dried at 100° contain :

Kind of Bark	Mixed alkaloids	Alkaloids soluble in ether	Pure quinine	Crystallized sulphate of quinine
<i>C. succirubra</i> .				
Original bark, 8 years old .	10.86	3.705	.793	1.057
Renewed bark, 2 years old.	10.40	7.654	4.653	6.204
" " "	9.154	5.707	2.754	3.672
" " "	10.67	3.142	1.413	1.884
" " "	8.606	3.307	1.382	1.843
" " "	8.176	2.973	1.185	1.680
" " "	10.37	4.193	2.024	2.700
<i>C. pahudiana</i> .				
" " "	2.51	1.038	0.032	—
Original bark . . .	2.023	1.324	0.606	0.808
Renewed bark, 2 years old.	4.80	2.362	0.783	1.044
<i>C. officinalis</i> .				
Renewed bark, 2 years old	10.86	4.228	2.804	3.738
" " "	6.944	2.244	1.273	1.697
" " "	6.734	2.670	1.681	2.241
" " "	4.288	2.080	0.825	1.100
" " "	3.72	3.297	2.600	3.466

A comparison of the first two analyses in this table shows that, whilst the amount of mixed alkaloids in the two barks is nearly the same, the amount of quinine in the renewed bark is very much greater. If this should prove to be a general rule, the millions of trees of *C. succirubra* now growing in British India might be adapted to produce large quantities of bark fit for the manufacture of quinine.

3. East India *Cinchona* Bark (B. H. Paul, *Pharm. J. Trans.* [3], vi. 321).

The following analyses refer to parcels of bark imported from Ceylon in 1875.

	<i>C. succirubra</i>							<i>C. officinalis</i>	
	19	20	21	22	23	24	25	26	27
Cryst. quinine sulphate .	1.42	1.69	1.59	1.85	1.62	2.31	2.37	6.08	5.03
Cryst. cinchonidine sulphate	3.46	3.46	2.70	4.10	4.97	0.63	0.38	0.98	trace
Cinchonine .	1.90	1.43	0.95	1.63	2.05	0.16	0.12	trace	0.13

All the samples were in a somewhat moister condition than is usually the case with cinchona bark, and the results apply to the bark dried at 100°. The average loss of weight by drying was about 10 per cent.

The following table gives results from Indian barks recently imported, but whether from the mainland or Ceylon is uncertain :

Kind of bark	Sulphates		Cinchonine
	Quinine	Cinchonidine	
East India Crown, renewed . . .	3.85	1.50	2.70
East India Crown . . .	5.20	0.82	—
" " . . .	4.3	1.5	0.23
" " . . .	4.5	1.6	0.18
" " renewed . . .	3.8	1.2	0.22
Red Bark, mossed . . .	1.72	—	1.70

4. *Cinchona* barks from Java (R. W. van Gorkom, *Pharm. J. Trans.* [3] iv. 341.)

<i>Cinchona</i>	Leaf	Locality	Planted	Water	Neutral tartrate acid	Quinine	Cinchonidine	Quinidine	Cinchonine	Amorphous alkaloid	Total alk. aloids	Quinine sul- phate calcd.
<i>Officialis</i>	Broad	Lembang	1870	12.77	6.35	2.33	3.13	none	0.71	0.80	6.97	6.13
"	"	Raoung-gunung	1868	13.32	6.25	3.27	1.59	trace	0.21	0.80	5.87	4.30
"	Average	"	"	12.77	8.34	5.19	1.58	"	0.86	0.20	7.83	6.98
"	Very small	"	"	13.07	7.90	5.86	0.74	"	0.62	0.45	7.67	7.89
"	Small, very pointed	"	"	13.37	7.20	5.42	0.89	"	0.44	0.64	8.89	7.29
"	Three varieties mixed	Kawak Tjiwidai	1869	13.74	3.87	1.75	1.38	"	0.34	0.26	3.73	2.35
"	Broad	"	1868	12.17	8.64	2.68	4.29	none	0.21	0.67	7.85	3.61
"	"	Rantia Bolang	"	9.07	5.35	2.71	1.61	trace	0.55	0.96	5.63	3.64
"	"	Tjiburrum	"	9.14	5.99	4.25	0.76	none	0.20	0.69	5.90	5.72
"	Small, very pointed	Raoung-gunung	"	14.48	10.36	5.92	2.47	"	0.19	0.91	9.49	7.98
<i>Calisaya</i> (Schuhkratt)	"	Lembang	1865	14.45	1.07	0.40	0.46	trace	2.74	0.63	4.23	0.56
" (crop)	"	Nagrak	"	13.32	4.18	1.80	1.56	0.40	0.32	0.17	4.25	3.42
" (Schuhkratt)	"	Tjomas	"	14.00	1.28	1.04	trace	0.48	2.03	0.66	4.21	1.40
" (crop)	"	Lembang	1867	13.59	1.43	0.56	0.59	trace	0.09	0.20	1.44	0.75
" (Ledger)	Long fruit	Nagrak	"	14.19	5.18	2.28	1.91	"	0.33	0.70	5.22	3.07
"	"	Tjiburrum	"	8.51	6.24	5.07	none	"	0.91	0.50	6.63	6.82
"	"	Raoung-gunung	"	13.85	4.90	3.88	"	"	1.02	0.96	6.85	5.22
"	"	"	"	14.41	10.88	8.83	"	"	0.10	0.91	9.84	11.88
"	"	"	"	14.73	11.20	9.90	"	"	0.17	1.21	10.47	12.23
<i>Caloptera</i> (seed plant)	"	"	"	8.63	2.65	1.83	0.27	"	0.17	0.79	3.06	2.46
" (crop of 1872)	"	Tjainuan	"	12.71	2.03	1.38	0.26	"	2.28	2.00	5.92	1.86
" (young plant)	"	"	1865	14.37	1.02	0.65	0.16	"	2.78	1.23	4.72	0.87
<i>Lancifolia</i> (from a dead tree)	"	"	"	13.25	2.66	0.79	1.35	"	0.72	0.47	3.33	1.06
"	"	"	"	7.10	6.08	4.75	0.19	0.08	0.83	1.03	6.96	6.39
<i>Succimura</i>	"	Lembang	1869	15.00	9.98	1.67	6.36	none	0.70	1.83	10.56	2.25
"	"	Kawak Tjiwidai	"	12.98	7.44	1.06	4.39	"	0.53	1.33	7.85	1.42
<i>Pahndiana</i>	"	Tjibodlas	"	13.20	1.24	0.30	0.73	"	trace	0.46	1.49	0.40

* This bark is from a tree which is probably identical with the *Cinchona officinalis* *Bomplandia* var. *angustifolia* of British India.

Effect of Manures on the Alkaloidal yield of Cinchonas (*Pharm. J. Trans.* [3], iii. 521). From experiments made by Mr. Broughton, the Government Quinologist at the Ootacamund Plantation, in the Department of Madras, it appears that the use of manures, either artificial or natural, increases the alkaloidal yield of the cinchonas. Some fine three-year-old plants of *Cinchona succirubra* were treated in November, 1869, in plots of fifty each, with 1 lb. of ammonium sulphate and the same quantity of guano. No perceptible increase in luxuriance or rapidity of growth was perceived to result, but in January, 1872, the difference in the alkaloidal yield of bark from the manured and non-manured plants was as follows:—

	Manured.	Unmanured.
Total alkaloids	7.25	4.89 per cent.
Quinine	2.45	1.78
Cinchonidine and Cinchonine	4.80	3.11

The stem-bark of trees manured with 1 lb. of guano gave the following results, as against trees not so treated:—

	Manured.	Unmanured.
Total alkaloids	5.29	4.76 per cent.
Quinine	0.91	1.04
Cinchonidine	4.38	3.72

The loss in quinine and small gain in total alkaloids may possibly be owing to the exciting action of the guano hastening the change, through which, as this species grows older, it loses its alkaloidal character. Mr. Broughton, therefore, does not recommend that *C. succirubra* should be manured, as the cost of manure would outweigh the small increased richness in the bark.

C. officinalis has always been noted for its extreme sensitiveness to situation, sunlight, and character of soil. Trees of this species, treated with 1 lb. of guano, although differing in no respect from unmanured trees while growing, yielded bark containing the following percentages of alkaloids:—

	Manured.	Unmanured.
Total alkaloids	6.51	3.98 per cent.
Pure Quinine	4.41	2.40
Cinchonidine and Cinchonine	2.10	1.58

Trees of the same species, treated with $\frac{3}{4}$ lb. ammonium sulphate, gave results as under:—

	Manured.	Unmanured.
Total alkaloids	5.76	4.54 per cent.
Pure Quinine	3.11	2.64
Cinchonidine and Cinchonine	2.65	2.00

From 1867 to 1872 trees of this species were treated with about four barrow-loads of farmyard manure each. In February, 1872, bark from trees so manured, and from similar trees unmanured, gave the following results:—

	Manured.	Unmanured.
Total alkaloids	7.49	4.68 per cent.
Pure Quinine	7.16	2.40
Cinchonidine and Cinchonine	0.34	2.28

Farmyard manure is therefore superior to artificial manure for this purpose, and favours the production of quinine over cinchonidine and cinchonine.

As no outward difference could be observed in the manured trees from those not so treated, Mr. Broughton is of opinion that the alkaloids are not specially active constituents in the processes connected with the life and growth of the plant.

Ash of Cinchona-barks.—The following determinations have been made by Carles (*Pharm. J. Trans.* [3], iii. 723).

	Huanoco		Calisaya		Succirubra	
Ash	1·831	1·885	1·350	1·361	1·402	1·741
Silica, soluble	0·263	0·241	0·023	0·032	0·020	0·031
„ insoluble	0·041	0·047	0·024	0·031	0·025	0·018
Alumina	0·061	0·050	0·030	0·020	0·062	0·052
Iron	0·061	0·042	0·065	0·049	0·053	0·070
Manganese	0·048	0·026	0·027	0·032	0·042	0·025
Lime	0·376	0·383	0·382	0·379	0·546	0·720
Magnesia	0·034	0·034	0·016	0·031	0·021	0·018
Potash	0·429	0·540	0·340	0·252	0·215	0·298
Soda	0·081	0·069	0·041	0·052	0·048	0·034
Copper	trace	trace	trace	trace	trace	trace
Carbonic acid	0·309	0·318	0·338	0·345	0·280	0·291
Sulphuric acid	0·027	0·034	0·036	0·038	0·035	0·034
Phosphoric acid	0·074	0·053	0·048	0·067	0·046	0·042
Chlorine	0·015	0·009	0·008	0·010	0·014	0·012

Carles also finds that cinchona-barks contain glucose, probably arising from the decomposition of cinchonotannic acid. The barks richest in alkaloids contain the smallest quantities of ammonia.

CINCHONA-BASES. *Detection and Estimation.*—For distinguishing the alkaloids of cinchona-bark one from the other, W. Stoddart (*Pharm. J. Trans.* [2], vi. 241) recommends the use of *potassium thiocyanate*. The precipitate thereby formed in a solution of quinine exhibits under the microscope the form of long slender needles; that of quinidine appears in round crystalline masses, and that of cinchonine in large well-defined prisms. This method has been further developed by F. Schrage (*Arch. Pharm.* [3], v. 504), who finds that under certain conditions it yields very characteristic results. The solutions of the alkaloids must be prepared without addition of free acid, at a temperature not more than 10° above that of the room. The solution of potassium thiocyanate should be very strong (equal parts of the salt and water), and in the case of very slightly soluble salts, such as sulphate of quinine, it is best employed in the solid form. If, with these precautions, a drop of the filtered solution of the alkaloid, and a drop of the thiocyanate solution, or a granule of the solid salt, be placed on the object stage of a microscope and covered with a small glass plate, so that the two may run together, and the whole be left at rest for half-an-hour, the liquid will exhibit a turbidity, which the microscope shows to consist of a mass of crystals. Quinine-salts exhibit thin spicules radiating from a centre; cinchonine-salts thicker rays diverging from one point like a fan; quinidine-salts, round drops attached to one another in chains like certain fungi.

Estimation of the total quantity of Alkaloids in Cinchona-barks.—1. Hager, in 1859 (*Zeitschr. anal. Chem.* viii. 477), published a method of estimation which consisted in digesting 10 grams of cinchona-bark for a short time with about 130 grams of water and 10 grams of potash-ley, sp. gr. 1·35, then adding 15 grams of sulphuric acid, sp. gr. 1·15, boiling for twenty minutes; adding water after cooling, so as to make up the liquid to 100 c.c.; filtering; and precipitating the measured filtrate with 50 c.c. of *picric acid solution* saturated in the cold. The molecular weight of cinchonine, being but little less than that of quinine and quinidine, the quantity of the alkaloids may be calculated with sufficient accuracy from the weight of the precipitate obtained from 100 c.c. of the filtered solution.

Objections have, however, been made to this method by van der Burg (*ibid.* ix. 305), first, because the extraction of the alkaloids is incomplete; secondly, because the precipitate is not of constant composition, foreign matters being carried down with the alkaloids.

O. Medin, however (*ibid.* xi. 447), finds, as the result of a large number of experiments, that the method is perfectly trustworthy, the extraction of the alkaloids being complete, their precipitation by picric acid also complete, and the small error arising from the simultaneous precipitation of other substances being compensated by a slight loss of the precipitated picrate during washing. Moreover the method is easy and expeditious.

2. The following method is given by de Vrij (*Pharm. J. Trans.* [3], iv. 241). 20 grams of the pulverised bark is made up into a paste with 5 grams of slaked lime;

the paste dried and twice boiled with strong alcohol; the solution acidulated with sulphuric acid; the alcohol distilled off; and the alkaloids precipitated with caustic soda, washed with water, dried, and weighed.

E. L. Cleaver (*ibid.* vi. 361) recommends this method of estimation as the best that has been hitherto proposed, but at the same time points out that it is defective in two respects, viz.: (1) the quantity of bark employed is too small; and (2) in the washing of the precipitated alkaloids, a considerable loss may occur in consequence of their solubility. To avoid these causes of error, Cleaver uses 100 grams of bark, and precipitates the solution of the sulphates, not with soda, but with baryta-water, then evaporates to dryness, and extracts the free alkaloids with alcohol.

The remainder of the process may be varied according to the object in view. If only the total amount of mixed alkaloids is required, this amount may be ascertained by evaporating a portion of the liquid and weighing the residue dried at 130°. But if the relative proportions of quinine and the other bases are to be determined, one of the following methods must be adopted:

a. A portion of the alcoholic extract is evaporated, the residue exhausted with ether, and the ethereal solution evaporated to dryness at 130°. The residue consists of quinine, the amount of which will thus be accurately determined, provided cinchonidine is absent; otherwise the result will be too high.

b. The alcoholic solution is divided into three or four equal parts. The first, evaporated to dryness and dried at 130°, gives the total amount of the alkaloids present. The second is evaporated to dryness, and the residue treated with ether as above: this gives the quinine. The third is titrated with sulphuric acid, and the proportions of the alkaloids calculated from the result according to the following equations. If the sum of the quantities of quinine and quinidine be denoted by x , the amount of cinchonine and cinchonidine together will be equal to the total amount of the alkaloids diminished by x , and the quantity of sulphuric acid used, S , will be given by the formula:

$$S = \frac{98}{648} x + \frac{98}{616} (\text{total alkaloids} - x)$$

whence x may be determined; and this diminished by the amount of quinine previously found gives the quantity of quinidine. Further, if the portion of the alkaloids which is insoluble in ether be dissolved in sulphuric acid, and the solution be made slightly alkaline with caustic soda and mixed with Rochelle salt, a precipitate of cinchonidine tartrate is obtained, containing 80.4 per cent. cinchonidine. Lastly, the cinchonine is estimated by difference.

3. J. C. Bernelet Moens (*Arch. Pharm.* [2], viii. 24) determines the amount of water in cinchona-bark by heating a gram of the powder sifted through silk gauze in a current of perfectly dry air heated to 125°. For the estimation of the alkaloids, 25 to 30 grams of the same powder are treated with lime and alcohol, as in de Vrij's method; and the bases are converted into sulphates, precipitated by caustic soda, and converted into hydrochlorides. The bases are next separated from one another by means of a solution of Rochelle salt, in which cinchonidine tartrate is nearly insoluble, whereas quinine tartrate dissolves in 1,500 parts of it, quinidine tartrate in 30 parts, cinchonine tartrate in about 35 parts at 24°. The resulting solution contains the last two salts and traces of the first two, together with an amorphous alkaloid and quinamine. The quinidine is easily separated from the cinchonidine in the form of hydriodide, that of the latter base only being easily soluble in water and in alcohol. The weight of the quinidine hydriodide, dried at 100°, gives, when multiplied by 0.7168, the quantity of the free base. From the hydriodide of cinchonine contaminated with the amorphous alkaloid, the cinchonine is separated by treating the weighed mixture with alcohol of 40 per cent., in which only the amorphous base is easily soluble. The method of separating quinine from cinchonidine varies to a certain extent according to the relative quantities of the two, but the separation may always be effected by ether, 1 part of cinchonidine requiring for solution 170 parts of this liquid. The cinchonidine still remaining attached to the quinine, may be removed by converting the bases into sulphates, and proceeding according to the relative solubilities of these two salts. The quinine sulphate is then to be dried at 120° and weighed: it contains 86.86 per cent. quinine.

Detection and Estimation of Quinine in a mixture of Cinchona-bases.—According to de Vrij (*Pharm. J. Trans.* [3], vi. 461), the best reagent for this purpose is the iodosulphate of quinidine, which, when added to a solution containing quinine, throws down a precipitate of quinine iodosulphate (herapathite), identical with that which is formed on adding iodine to quinine sulphate. To prepare the test-solution, 2 parts of quinidine sulphate are dissolved in 8 parts of water containing 5 per cent. of sulphuric acid. To this solution 100 parts of water containing 2 parts of potas-

sium iodide and 1 part of iodine are slowly added, with constant stirring. The orange-coloured precipitate thereby formed rapidly coheres, on slight elevation of temperature, to a brown-red resinous substance from which the supernatant liquid (which still contains a little quinoidine sulphate) is poured off; and the resinous body after being washed by heating with distilled water on the water-bath, is finally dried at 100° , at which temperature it is soft and tenacious, but becomes brittle on cooling. One part of this substance is heated with 6 parts of alcohol of 92–94 per cent. until it is dissolved; the solution poured off from a portion which separates on cooling is evaporated to dryness; and the residue is treated with 5 parts of cold alcohol. A portion then remains undissolved, and is separated by filtration from the clear dark solution, which constitutes the reagent.

For the determination of the quinine in a specimen of mixed alkaloids from a cinchona-bark, 1 part of the alkaloids is dissolved in 20 parts of alcohol of 90–92 per cent. containing 1·6 per cent. of sulphuric acid; and the quinine is separated from this solution by the gradual addition of the alcoholic solution of quinoidine iodosulphate, the slightest excess of which, after the total precipitation of the quinine, imparts a deep yellow colour to the liquid. The vessel containing the liquid and precipitate is heated on a water-bath until the liquid begins to boil; then, after cooling, the vessel is weighed (to ascertain the weight of the solution, in order to make correction for the slight solubility of the precipitated iodosulphate of quinine). The precipitate is now filtered, and washed with a saturated solution of quinine iodosulphate,* and the weight of the funnel and moist filter-paper ascertained; the filter is then dried, and the weight again taken; and the amount of quinine iodosulphate corresponding with the quantity of solution which remained upon the filter-paper is deducted from that corresponding with the quantity contained in the original filtrate, the balance being added to the weight of the precipitate, which is removed from the filter-paper and dried at 100° until the weight is constant. 1 part of quinine iodosulphate corresponds with 0·5609 per cent. of anhydrous quinine, or with 0·7245 of crystallised quinine disulphate.

The success of this method depends upon the fact that quinine is wholly precipitated by the iodosulphate of quinoidine before any of the other alkaloids are affected; if, however, the proportion of cinchonidine in the mixed alkaloids is large relatively to the quinine, it becomes necessary to add the test-liquid very carefully, and keep the solution continuously stirred, as otherwise an orange-coloured gelatinous precipitate of cinchonidine iodosulphate will be formed before the complete separation of the quinine. Should this happen, the liquid must be heated until the precipitate is redissolved, before continuing the addition of the test-solution.

Another method of determining the amount of quinine in mixtures of various kinds is described by A. H. Allen (*Pharm. J. Trans.* [3], vi. 964). The liquid concentrated to about 10–16 c.c. is placed in a cylindrical vessel; ammonia is added in sufficient quantity to make its odour perceptible; and the whole is covered with an equal volume of ether. The vessel is tightly closed, and the contents shaken together several times, whereupon the quinine is set free by the ammonia dissolves in the ether. The vessel is then left at rest till the liquids have separated; the ether is pipetted off; the entire process is repeated once or twice; and the ethereal solution is evaporated. The residue has a tolerably constant composition, not, however, that of quinine trihydrate, $C^{20}H^{24}N^2O^3 + 3H^2O$, but nearly that of the monohydrate, from which, however, it differs by about 1 p. c. water. The weight of this residue multiplied by the factor 1·289 gives that of the corresponding sulphate, $C^{20}H^{24}N^2O^3 \cdot 2H^2SO^4 + 7H^2O$. This method, as shown by numerous experiments, gives satisfactory results, and may be applied, for example, to the estimation of quinine in the mixture of its citrate with citrate of iron.

According to A. N. Palmer (*Pharm. J. Trans.* [3], vii. 89), the ether in this process may in many cases be advantageously replaced by chloroform. The experiments show that neither the excess of alkali required to precipitate the quinine, nor the presence of glycerin or sugar in the liquid, interferes in any way with the accuracy of the process. If the quinine salt is mixed with ammonium citrate, it is best to agitate the precipitated quinine with chloroform, as the base is not completely extracted from aqueous solution by ether. Attention to this point is important in the estimation of quinine in the citrates of quinine and of iron-quinine, as these salts are almost always mixed with ammonium citrate.

Perret (*Dent. Chem. Ges. Ber.* vii. 735) determines the amount of quinine in cinchona bark by means of sodium silicate, which dissolves the alkaloids without altering them. 10 grams of the bark are heated with 60 grams of 90 per cent. alcohol containing 5 grams of a strongly alkaline solution of water-glass of 40° Bm.;

* Alcohol of 92 per cent., at $24^{\circ}5'$, dissolves 0·133 per cent. of the qui

the liquid is filtered after ten minutes; and these operations are twice repeated, first with 80 gr. alcohol and 2.5 gr. water-glass, secondly with 80 gr. alcohol. The united filtrates are evaporated to a syrup, and exhausted with ether; the residue left on evaporation of the ether is acidulated with sulphuric acid; and the resulting quinine sulphate is either weighed as such, or precipitated as oxalate.

Quinine may be distinguished from other cinchona alkaloids, by agitating 1 part of the sulphate to an emulsion with 10 parts of water at 12° – 16° , leaving the liquid at rest for half-an-hour, then filtering and adding 7 c.c. of ammonia-solution, sp. gr. 0.86 to 5 c.c. of the filtrate. If the quinine salt is pure, no precipitation will take place; but if other alkaloids are present, a precipitate will be formed—in the case of cinchonidine with not more than 1 part in 100 (Hesse, *Deut. Chem. Ges. Ber.* x. 2152).

CINCHONINE GROUP.

Cinchonine, $C^{20}H^{21}N^1O$. This base boiled with an aqueous solution of chloride, sulphate, or oxalate of ammonia, is dissolved with evolution of ammonia (Hesse, *Liebig's Annalen*, clxxvi. 217). It separates from alcohol in anhydrous crystals, gives no fluorescence in sulphuric acid solutions: its *hydrochloride*, $C^{20}H^{21}N^1O.HCl + 2H^1O$, crystallises in long needles; the *acid sulphate*, $C^{20}H^{21}N^1O.H^1SO^4 + 2H^1O$, in compact prisms (Hesse, *Deut. Chem. Ges. Ber.* x. 2152).

Iodine-compounds.—By rubbing together 2 pts. of cinchonine with 1 pt. of iodine, treating the mass with ordinary alcohol, and evaporating the alcoholic solution, yellow needles are obtained consisting of the hydriodide, $C^{20}H^{21}N^1O.HI + H^1O$. The residue, which is insoluble in ordinary alcohol, dissolves in absolute alcohol, and from this solution water throws down a saffron-yellow crystalline precipitate, consisting of the di-iodide, $C^{20}H^{21}N^1O.II^2 + 2H^1O$. The tri-iodide, $C^{20}H^{21}N^1O.II^3$, is obtained by treating cinchonine sulphate with iodine dissolved in potassium iodide, dissolving the precipitate which forms in alcohol, and evaporating the liquid (H. R. Bauer, *Arch. Pharm.* [3], v. 289).

The same salt is formed by oxidising an alcoholic solution of cinchonine hydriodide, or by mixing such a solution with iodine dissolved in alcohol, and separates in splendid brown tabular crystals belonging to the rhombic system and having the composition $C^{20}H^{21}N^1O.II^3 + H^1O$ (Jørgensen, *J. pr. Chem.* [2], iii. 146).

Methylcinchonium tri-iodide, $C^{20}H^{21}N^1O.CH^3I^3$, forms dark brown leaflets having an adamantine lustre, moderately soluble in hot alcohol, melting at 161° – 162° . **Ethylcinchonium tri-iodide**, $C^{20}H^{21}N^1O.C^2H^5I^3$, crystallises in dark brown prisms melting at 141° – 142° (Jørgensen).

Cinchonine Sulphatoperiodides (Jørgensen, *J. pr. Chem.* [2], xiv. 356). $8C^{20}H^{21}N^1O.6SH^1O^4.6HI.I^1.12H^1O$ is formed by dissolving 2 mols. of cinchonine, 1 of sulphuric acid and 2 of hydriodic acid in hot alcohol, and adding 2 at. of iodine. It is so easily decomposed that it must be washed with ice-cold strong alcohol, and at once dried by pressure and over sulphuric acid. It begins to lose water at 70° , melts at 140° – 145° , and is perfectly decomposed at 170° with formation of chinoline. It is easily soluble in hot alcohol, but is not affected by ether, chloroform, or bisulphide of carbon. It forms a double salt with mercuric iodide.

$4C^{20}H^{21}N^1O.2SH^1O^4.4HI.I^1$ is obtained by dissolving cinchonine in boiling alcohol, with addition of the calculated quantity of sulphuric acid and hydriodic acid, and for each molecule of cinchonine at the most 2 atoms of iodine. Attempts to recrystallise this body produce a mixture of the previous and the following compounds; possibly also cinchonine tri-iodide is formed at the same time. Ether and bisulphide of carbon are both slightly coloured by this compound when hot: chloroform is not affected by it. An alcoholic solution gives with mercury a subiodide and a double iodide.

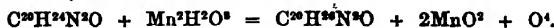
$2C^{20}H^{21}N^1O.SH^1O^4.2HI.I^1$ is probably identical with the cinchonine salt obtained by Herapath, and may be prepared in several ways, e.g., by dissolving the theoretical quantities of the constituents in hot alcohol, and precipitating by addition of water. It is slightly soluble in ether, carbon sulphide, and chloroform, but dissolves with moderate facility in hot alcohol. With mercury it behaves like the preceding salt.

Thiocyanate.—Potassium thiocyanate, added to a concentrated aqueous solution of cinchonine hydrochloride at ordinary temperatures, forms a white curdy precipitate. If, however, the solution is warmed, and, if possible, somewhat diluted, the cinchonine thiocyanate separates in six-sided prisms or in four-sided leaflets perpendicularly truncated or bevelled at the ends. The salt dissolves in 474 pts. of water at 20° , with moderate facility in boiling water and in alcohol. The precipitation of cinchonine from its neutral solutions by a slight excess of potassium thiocyanate is so complete,

that the filtrate gives no precipitate with ammonia (Hesse, *Liebig's Annalen*, cxxx. 51). According to Schrage (*Arch. Pharm.* [3], v. 501), when drops of highly concentrated solutions of potassium thiocyanate and a cinchonine salt are brought in contact under a microscope, fan-shaped groups of crystals gradually form, sometimes collected round an elongated axis, like the foliage of an *Equisetum*.

With *phenol*, cinchonine salts form oily compounds, which dissolve easily in water, and are precipitated from the solution by further addition of phenol-water (Hesse).

Hydrocinchonines. Willm a. Caventou, by treating cinchonine with potassium permanganate, obtained, together with other compounds, a hydrocinchonine having the composition $C^{20}H^{22}N^2O$ (1st *Suppl.* 464). According to Hesse (*Liebig's Annalen*, clxvi. 217), this body is formed by the reaction:



Hydrocinchonine thus obtained crystallises in shining colourless prisms soluble in alcohol to about the same extent as cinchonine. It dissolves in 534 parts of ether at 20°, and in 1300 parts of water at 16°. In boiling water it dissolves to a considerable extent, the greater part separating in small prisms on cooling. The alcoholic solution has a basic reaction, and is easily neutralised by acids. The neutral salts crystallise well. The *hydrochloride* forms colourless prisms easily soluble in water, and likewise crystallising in small prisms. The *hydriodide* also crystallises in white prisms, which dissolve sparingly in solution of potassium iodide, moderately in water, and very easily in alcohol. The *neutral sulphate* resembles ordinary sulphate of cinchonine both in form and in solubility; the *neutral* and *acid tartrate* also resemble the corresponding cinchonine salts. When the tartrate in aqueous solution is mixed with excess of sodium carbonate, the hydrocinchonine separates in crystalline nodules in proportion as the carbonic acid escapes: hence tartaric acid does not hinder the precipitation of hydrocinchonine. When the solution of the base in dilute sulphuric acid is mixed with a solution of potassium permanganate, the latter is slowly decolorised at ordinary temperatures (Hesse).

The same, or an isomeric base is formed, together with a more highly hydrogenised compound, $C^{20}H^{24}N^2O$, by the action of nascent hydrogen on cinchonine. When a strongly acid solution of cinchonine acetate is treated with sodium-amalgam, hydrogen is evolved, slowly at first, rapidly after further addition of the amalgam, and an oily liquid separates, the quantity of which increases on cooling. This oil dissolves in water, and on adding ammonia to the solution, a white precipitate is formed, separable by ether into two parts, the larger portion being insoluble in that liquid. This insoluble portion dissolves readily in alcohol, especially at the boiling heat, and may be obtained by repeated crystallisation from the alcoholic solution, in brightly shining scales having the composition $C^{20}H^{24}N^2O$ (W. Zorn, *J. pr. Chem.* [2], viii. 275).

By treating the base with a quantity of dilute sulphuric acid not sufficient to dissolve the whole of it, a solution is obtained which on cooling deposits long crystalline needles having the composition of the *anhydrous neutral sulphate*, $(C^{20}H^{22}N^2O)^2 \cdot H^2SO^4$.

When crystallised hydrocinchonine is heated with *ethyl bromide* to 100° in sealed tubes, the contents become red and soluble in water, and the aqueous solution leaves on evaporation a deep red syrupy mass. Absolute alcohol dissolves a portion of this product, leaving a white powder very soluble in water, and the resulting aqueous solution deposits on evaporation large colourless rhombohedrons of the compound $C^{20}H^{22}N^2O \cdot 2C^2H^5Br$, or $C^{20}H^{22}(C^2H^5)^2N^2O \cdot Br^2$, designated by Zorn as *diethyl-cinchonine dibromide*. This compound is distinguished from ethyl-cinchonine bromide by its solubility in water and insolubility in alcohol. Its solution is not precipitated by alkalis, but the alkaline liquid quickly turns brown and decomposes. The solution of the dibromide digested with moist silver oxide yields a strongly alkaline liquid, which, however, immediately decomposes in a similar manner.

Amorphous Hydrocinchonine. $C^{20}H^{22}N^2O$, is formed in small quantity, together with crystalline hydrocinchonine, by the action of sodium-amalgam on cinchonine dissolved in acetic acid, and constitutes the portion of the ammonia precipitate which is soluble in ether. By a slight modification of the process it may be obtained in larger quantity. A solution of cinchonine acetate mixed with a quantity of alcohol sufficient to retain in solution all the cinchonine that is set free at the boiling heat, is subjected to prolonged treatment with sodium-amalgam, and the hot alkaline liquid thereby produced is mixed with an equal volume of water, whereby an oily layer is immediately separated, the quantity of which increases considerably on cooling. This oil dissolves almost completely in ether, the slight residue consisting of crystallised hydrocinchonine, a small quantity of which, however, is dissolved by the ether; the amorphous base may be freed from it by redissolution in a small quantity of ether.

The ethereal solution, which has a beautiful violet fluorescence, leaves the base $C^{20}H^{22}N^2O$, on evaporation, in the form of a yellowish perfectly amorphous mass having a faint sweetish taste. All its compounds and derivatives are likewise perfectly amorphous.

The tetranitro-derivative, $C^{20}H^{24}(NO^2)_4N^2O$, is formed by gradually adding red fuming nitric acid to a solution of the base in dilute nitric acid, and separates on addition of water, as a yellow amorphous powder nearly insoluble in alcohol, ether, and benzene, soluble in concentrated acids, and separated therefrom by water. When heated it does not explode, but takes fire and burns quickly, leaving a slowly combustible cinder. It may be amidated by treatment with tin and hydrochloric acid, but the resulting compound is not of a character to admit of exact investigation.

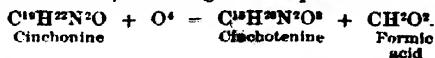
Action of Ethyl Bromide on Amorphous Hydrocinchonine.—This base heated to 100° in sealed tubes with ethyl bromide yields an amorphous mass soluble in water and forming a strongly acid solution from which ammonia throws down a white earthy precipitate; this, however, quickly decomposes, so that it is not possible to obtain the compound in the pure state. The ethylation appears to be incomplete, even after repeated treatment of the precipitate with ethyl bromide.

By subjecting the salt obtained after twice-repeated treatment with ethyl bromide to the action of fuming nitric acid, a nitro-derivative is obtained having the composition $C^{20}H^{22}(C^2H^5)(NO^2)_2N^2OBr^2$, and differing from the nitro-derivative of crystallised hydrocinchonine in being less easily combustible and not being coloured by ammonia. Its formation may be explained by supposing that the action of ethyl bromide on amorphous hydrocinchonine first gives rise to the compound $C^{20}H^{22}(C^2H^5)^2N^2O \cdot 2HBr$, and that by the further action of ethyl bromide on the base $C^{20}H^{22}(C^2H^5)^2N^2O$ precipitated therefrom by ammonia, the compound $C^{20}H^{22}(C^2H^5)^2N^2O \cdot 2C^2H^5Br$, or $C^{20}H^{22}(C^2H^5)^2N^2OBr^2$, is formed, which by substitution of $4NO^2$ for H^4 yields the compound above formulated (Zorn).

Hexchlorhydrocinchonine, $C^{20}H^{22}Cl^6NO$ (according to Hesse).—This compound is formed, with great evolution of heat, when chlorine gas is passed into a solution of amorphous hydrocinchonine in hydrochloric acid; the liquid acquires a deep reddish-yellow colour, and when mixed with water yields a bulky yellow precipitate, which, after washing with absolute alcohol, has the composition $C^{20}H^{22}Cl^6NO + \frac{1}{2}H^2O$. It dissolves easily in strong acids, and is reprecipitated by water; easily also in alcohol and in ether: it appears to be quite incapable of crystallisation. It is decomposed by heat, but the chlorine which it contains appears to be very intimately combined, not being precipitated by silver nitrate.

The action of chlorine on amorphous hydrocinchonine likewise gives rise to a volatile decomposition-product which imparts an aromatic odour to the liquid remaining after the chlorhydrocinchonine has been precipitated by water. This volatile compound may be extracted from the liquid by means of ether free from alcohol, and purified by evaporating the ether and distilling the residue with steam. It crystallises in slender needles which melt at 135° , and dissolve very easily in alcohol, less in ether, but are insoluble in water. This compound has the composition tetrachlorocryptidine. The reaction by which it is produced is not yet understood, but its formation justifies the conclusion that cinchonine contains an 11-carbon radicle, and that the bodies of the quinoline series are intimately related to cinchonine.

Skraup (*Deut. Chem. Ges. Ber.* xi. 311) takes a different view of the composition and relations of the hydrocinchonines. His analyses of cinchonine lead to the formula $C^{20}H^{22}N^2O$,* originally proposed by Laurent (i. 94); and he finds that the chief products of the oxidation of cinchonine by permanganate are cinchotennine (1st Suppl. 464) and formic acid, according to the equation:



This equation, however, does not explain the evolution of oxygen, which, according to Skraup's own observation, is an invariable concomitant of the reaction.

By the action of sodium-amalgam on cinchonine dissolved in acetic acid, Skraup, like Zorn, obtains two hydrocinchonines, one crystalline, the other amorphous, the proportions of the two produced varying according to those of the materials employed. When the proportion of sodium-amalgam was such as to yield between 3 and 4 at. H. to 1 mol. cinchonine, the product consisted almost wholly of the more highly hydrogenised amorphous base; and with 1-2 at. H. to 1 mol. cinchonine, the quantities of crystalline and amorphous hydrocinchonine obtained were nearly equal. Hence

* Hesse thinks it most probable that he was dealing with homocinchonine.

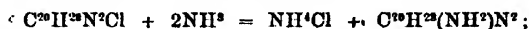
Skraup concludes that the amorphous base must be formed by assumption, not of 4H, as it should according to Zorn's formula, but of only 2H. The difficulty of obtaining this compound in the pure state has hitherto prevented the determination of its formula by exact analysis; but the analyses made favour the conclusion that it contains only 19C.

The analyses of crystallised hydrocinchonine and of its platinumchloride lead to the empirical formula $C^{19}H^{22}N^2O$, whence Skraup infers that this base must be dihydrocinchonine, $(C^{19}H^{22}N^2O)^2H^2$, formed by the union of two cinchonine-molecules with addition of 2 at. hydrogen. This view is in accordance with the fact, also observed by Skraup, that the crystallised base is not converted into the amorphous base by the action of nascent hydrogen.

Similar results are obtained by acting on cinchonine with zinc and dilute sulphuric acid, excepting that the hydrogenation is altogether less complete, and the proportion of crystallised hydrocinchonine larger.

Chlorocinchonide, $C^{20}H^{23}N^2Cl$ (W. Zorn, *J. pr. Chem.* [2], viii. 279). This compound, derived from cinchonine by substitution of Cl for HO, in the same manner as chlorocodide from codeine (1st Suppl. 480), is produced by heating cinchonine hydrochloride to 140° – 150° in sealed tubes for several hours with highly concentrated hydrochloric acid, prepared by saturating ordinary strong hydrochloric acid cooled by ice and salt with dry hydrogen chloride; by hydrochloric acid of ordinary strength the cinchonine is converted into the isomeric base cinchonidine. On opening the tube and evaporating the contents, hydrochloride of cinchonidine is obtained, from which the base itself may be precipitated by ammonia in shining crystalline scales having the composition $C^{20}H^{23}N^2Cl.H^2O$. The water of crystallisation is not given off at 120° , and at higher temperatures decomposition takes place. The hydrochloride, $C^{20}H^{23}N^2Cl.2HCl.H^2O$, dissolves in about 20 parts of water, and crystallises therefrom in transparent six-sided prisms, which become opaque when moistened with pure water, but recover their transparency in contact with hydrochloric acid. It is but slightly soluble in moderately concentrated hydrochloric acid, and is thrown down as a crystalline powder when its solution in the strong acid is diluted with water. The aqueous solution has a strong acid reaction, and exhibits all the properties of cinchonine hydrochloride except its fluorescence. The crystals do not give off their water at 120° , but suffer decomposition at higher temperatures.

Chlorocinchonide is not reconverted into cinchonine by heating with water or with alcoholic potash, neither does the chlorine appear to be replaceable by cyanogen. Heated to 150° – 160° in sealed tubes with alcoholic ammonia it dissolves, with separation of ammonium chloride, indicating a reaction expressible by the following equation:



but no decisive evidence of the formation of amidocinchonide has yet been obtained.

Attempts to replace the chlorine in chlorocinchonide by hydrogen, and obtain the compound $C^{20}H^{24}N^2$ (cinchonine *minus* oxygen), did not yield the expected result. When an alcoholic solution of chlorocinchonide was treated for some time with sodium-amalgam, and the resulting liquid mixed with water, microscopic crystals separated, consisting of a compound isomeric with chlorocinchonide, and at the same time there was formed an uncrystallisable compound soluble in ether, and yielding a nitro-derivative having the composition $C^{20}H^{22}(NO^2)^2N^2Cl$: hence it appears probable that the compound soluble in ether is an addition-product of chlorocinchonide, viz., $C^{20}H^{27}N^2Cl$ (Zorn).

Bromocinchonines (A. Kopp, *Arch. Pharm.* [3], ix. 34). Monobromocinchonine, $C^{20}H^{23}BrN^2O$, is prepared by dissolving cinchonine hydrochloride in dilute alcohol, and mixing the solution with rather more than the calculated quantity of bromine dissolved in alcohol. On adding ammonia till the red colour of the liquid changes to yellow, crystals of monobromocinchonine separate out. Sesquibromocinchonine, $C^{20}H^{21}Br^2N^2O$, is obtained by treating cinchonine with excess of bromine at ordinary temperatures. Dibromocinchonine, $C^{20}H^{19}Br^2N^2O$, is produced by boiling the hydrochloride of cinchonine with excess of bromine, and is obtained in laminar crystals by boiling the resulting resinous mass with water. These three bromocinchonines melt at nearly the same temperature, and decompose at the following temperatures:

Mono.	Sesqui.	Di.
above 230°	at 180°	at 200°

Oxycinchonines. Mono-, sesqui-, and di-oxycinchonine are prepared by boiling the corresponding bromocinchonines with alcoholic potash and water, precipitating with water, and repeatedly treating the precipitate with potash, and may be purified

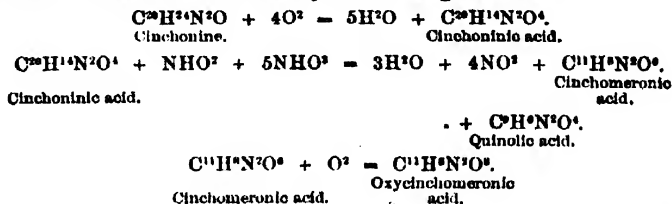
by saturating the solution with carbonic acid, evaporating, exhausting with water, and crystallising the residue from alcohol.

Monoxycinchonine, $C^{20}H^{21}N^1O^2$, crystallises in prisms; *sesquicycinchonine*, $C^{30}H^{31}N^1O^3$, and *dioxycinchonine*, $C^{30}H^{31}N^1O^4$, in feathery crystals. These compounds are white when recently prepared, but turn yellow on exposure to the air. They dissolve readily in alcohol, less easily in ether, are insoluble in water. Their acid solutions are not fluorescent. Their salts are difficult to crystallise. They are not sublimable, and turn brown at 205° , 208° , and 220° respectively. They are not coloured green by chlorine-water and ammonia, or red with potassium ferrocyanide and ammonia. They form white precipitates with tannic acid, brown with potassium periodide, yellow with platonic chloride. By the action of acetic anhydride at high temperatures, they are converted into brown greasy masses. The rotatory power of the three oxycinchonines in Hesse's mixture of chloroform and alcohol is:

	Monoxy.	Sesquiox.	Dioxy.
$\alpha =$	+ 193.93	+ 271.14 *	+ 214.34

Acids produced by Oxidation of Cinchonine (H. Weidel, *Liebig's Annalen*, clxxiii. 76).

Cinchonine treated with nitric acid of sp. gr. 1.4 yields a mixture of four acids, the relative proportions of which vary with the strength of the acid, and the duration of the action. These acids are formed by the following reactions:



Cinchonine in half kilograms at a time, is heated with ten parts of nitric acid in a capacious retort; in an hour the mixture begins to boil, and an energetic reaction sets in, the liquid becoming dark orange-yellow; the source of heat should be removed till this stage is over; finally the whole is boiled for 70 to 80 hours, until a sample diluted with water and supersaturated with ammonia, gives a clear solution, the precipitate first thrown down being re-dissolved by the excess of ammonia. The excess of acid is then distilled off, and the residue evaporated to a syrup, diluted with a little water, and then disseminated through 4 to 6 litres of water. After 24 hours, a clear liquid, A, and a yellow precipitate, B, are obtained. The aqueous solution, A (together with the wash-waters of B) is treated with ether, whereby a solution is obtained, which leaves on evaporation an indistinctly crystalline, slightly coloured mass, C. The aqueous liquor thus exhausted by ether, and left to itself for several days, deposits crystals, D; and the mother-liquors of these, when evaporated, give another crop of needles, E, whilst the last mother-liquors, F, are uncrystallisable.

B and C consist chiefly of quinolic acid; the mixed substances are dissolved in hot, strong, hydrochloric acid, and filtered from a little resin; on cooling crystals form, consisting of a hydrochloride of quinolic acid, stable only in presence of strong hydrochloric acid, and completely decomposed by water; these are dissolved in dilute hydrochloric acid; the solution, after treatment with animal charcoal and filtering, deposits slender needles of pure quinolic acid.

D is purified by dissolving it in hot dilute nitric acid, filtering after boiling with animal charcoal, whereby resin is removed, and leaving the solution to crystallise; the crystals are dissolved in a large bulk of boiling water, and treated with milk of lime, until the liquor is only feebly acid. The precipitate contains much calcium oxycinchomerate, some of which salt also crystallises from the filtrate on cooling. The calcium salts are dissolved in hot dilute hydrochloric acid, from which solution oxycinchomeronic acid crystallises in transparent tables. The filtrate from the crystals of calcium salt is evaporated, and treated with hydrochloric acid, when cinchomeronic acid separates in crystals; this is the least soluble of all the cinchonine

* Probably a misprint for 171.14, since Kopp remarks that the rotatory power of the oxycinchonines is as a general rule less than that of cinchonine, which, according to his measurement, is +227.30°.

oxidation-products. This first product is purified by crystallisation; finally transformed into copper-salt by addition of copper acetate to the hot aqueous solution, and decomposed by sulphuretted hydrogen.

E consists chiefly of cinchoninic acid, and is purified by recrystallisation from water, and treatment with animal charcoal.

F contains cinchoninic and cinchomeronic acids, separable by saturation with ammonia, filtration from resin, treatment of the filtrate with silver oxide, and of the silver salt thus formed with hydrochloric acid, whereby a solution is obtained, which gives a crystalline mass on evaporation; part of this remains undissolved on boiling with a moderate quantity of water; this is cinchomeronic acid.

Cinchoninic Acid separates from aqueous solutions which have been boiled for some time, in anhydrous crystals resembling caffeine; from solutions which have not been boiled, in well-defined prismatic crystals containing 4 mols. of water. By slow evaporation hydrated tabular crystals are obtained. The hydrated acid effloresces, dissolves slowly in alcohol, not at all in ether, in water only after long boiling, easily in dilute acids. The anhydrous acid is more easily dissolved by water. The solution is strongly acid, decomposes carbonates, and is precipitated by basic, but not by neutral acetate of lead, the precipitate being soluble in excess of the reagent and in a large quantity of water. The calcium salt, $C^{20}H^{12}CaN^2O^4 + 1\frac{1}{2}H_2O$, is slightly soluble in hot, nearly insoluble in cold water. The copper salt is anhydrous, forms violet-blue leaflets, and is very sparingly soluble in water. The silver salt, $C^{20}H^{12}Ag^2N^2O^4$, is not characteristic. The potassium salt, $C^{20}H^{12}K^2N^2O^4 + H_2O$, crystallises in cauliflower-like masses. The solution of the acid in hydrochloric acid forms with *platinic chloride* the salt $C^{20}H^{12}N^2O^4 \cdot 2HCl \cdot PtCl_4$, which crystallises in long, orange-red, sparingly soluble needles.

Cinchoninic acid when heated, melts and sublimes with partial decomposition, and burns with a bright flame. The calcium salt when heated gives off the odour of the quinol-bases. The acid heated with nitric acid is completely resolved into quinolic and cinchomeronic acids.

Quinolic Acid, $C^9H^8N^2O^4$, forms light, woolly, anhydrous crystals, resembling quinine sulphate; it tastes sour at first, then bitter, and is but little soluble in alcohol, and insoluble in ether and water, except in presence of a mineral acid or acetic acid. Caustic potash and ammonia colour it bright carmine-red, the colour disappearing however spontaneously or on addition of water. The silver salt, $C^9H^8Ag^2N^2O^4$, is crystalline and not altered by light; the other salts crystallise badly, and are difficult to purify. With *hydrochloric acid* quinolic acid forms the compound $C^9H^8N^2O^4 \cdot HCl$, which is decomposed by water, and forms with *platinic chloride* the compound $2(C^9H^8N^2O^4 \cdot HCl) \cdot PtCl_4$, which separates in needles of a fine dark orange-red colour.

Quinolic acid when heated behaves like cinchoninic acid. Fused with *potash*, it yields potassium nitrite. With *tin and hydrochloric acid* it forms a resinous amido-product. Heated with twice its weight of water and an equal quantity of *bromine* in a sealed tube, with repeated addition of bromine, it forms a resinous product, which when recrystallised from alcohol, distilled, and again crystallised, forms nearly colourless needles melting at $88^\circ-90^\circ$, and having the composition C^9HBr^2N . This compound, treated with sodium-amalgam, yields an oil soluble in ether, and having all the properties of chinoline.

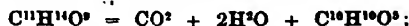
Cinchomeronic Acid, $C^{11}H^8N^2O^8$, dissolves most easily in very dilute nitric acid, and crystallises therefrom in crusts and nodules composed of small needles; in ether and in alcohol it is nearly insoluble. When heated it behaves like the two preceding acids. The calcium salt, $(C^{11}H^8N^2O^8)^2Ca + 10H_2O$, and the barium salt, $(C^{11}H^8N^2O^8)^2Ba + 4H_2O$, obtained by precipitating the ammoniacal solution of the acid with the corresponding chlorides, are crystalline precipitates dissolving with difficulty in water and giving off their water of crystallisation at 120° . The copper salt, $(C^{11}H^8N^2O^8)^2Cu$, separates on adding cupric acetate to a solution of the acid in acetic acid, as a sky-blue crystalline anhydrous precipitate nearly insoluble in water. The silver salt, $C^{11}H^8N^2O^8Ag^2$, obtained by precipitation, is not much affected by light.

Cinchomeronic acid fused with caustic potash does not yield potassium nitrite. Bromine and water convert it into a yellow, crystalline, difficultly purifiable substance containing bromine and nitrogen. Heated with nitric acid in sealed tubes, it is converted into oxycinchomeronic acid. Its calcium salt is decomposed by distillation, yielding pyridine.

Oxycinchomeronic acid, $C^{11}H^8N^2O^8$, crystallises in distorted, highly lustrous leaflets, considerably soluble even in cold water, easily soluble in alcohol, insoluble in ether. Its solutions are coloured blood-red by ferrous sulphate, the colour disappearing on addition of a free acid. The acid contains water of crystallisation, which it gives off at 120° .

The *potassium salt*, $C^{11}H^4K^1N^2O^8$, is very hygroscopic; the *silver salt*, $C^{11}H^4Ag^1N^2O$, darkens on exposure to light or when dried; the *calcium salt*, $(C^{11}H^4N^2O^8)^2Ca^2$, form dull sandy crystals nearly insoluble in water; the *copper salt*, $(C^{11}H^4N^2O^8)^2Cu^2$, is a gummy amorphous precipitate.

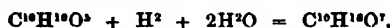
Pyrocinchonic Acid, $C^{10}H^{10}O^8$, is formed by the dry distillation of cinchonic acid:



it passes over in the form of an oil, solidifies after a while, and may be obtained by pressure, re-distillation, and crystallisation from ether, in well-defined tabular crystals.

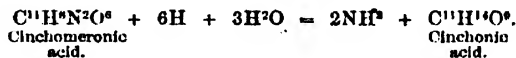
Pyrocinchonic acid is more soluble in ether and alcohol than in water, has a sweet taste and acid reaction, melts at 95° , volatilises with aqueous vapour, and behaves to metals like cinchonic acid, yielding salts having the composition $C^{10}H^7M^2O^8$. With melting potash, it yields oxalic acid and some of the lower fatty acids, and when boiled with chromic acid solution it gives off carbon dioxide and acetic acid. It is not acted on by acetyl chloride.

Hydropyrocinchonic acid, $C^{10}H^{10}O^7$, is formed by boiling an alcoholic solution of pyrocinchonic acid with sodium-amalgam:



and may be obtained in dull flat needles by neutralising the product with sulphuric acid and exhausting with ether. It melts at 170° , and forms a crystalline silver salt, $C^{10}H^{10}Ag^2O^7$.

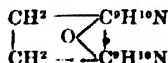
Cinchonic Acid, $C^{11}H^{14}O^8$. Cinchomeronic and oxycinchomeronic acid, when treated with nascent hydrogen, give off the whole of their nitrogen in the form of ammonia, the former being converted into cinchonic acid, the latter probably also into the same compound:



To prepare cinchonic acid, a solution of cinchomeronic acid in potash is boiled with sodium amalgam as long as ammonia is given off; the solution neutralised with acetic acid is precipitated with basic lead acetate; the precipitate is decomposed with hydrogen sulphide; and the acid solution decolorised with animal charcoal is evaporated to a syrup. It then, often only after several months, yields very deliquescent crystals, which may be purified by recrystallisation from ether.

Cinchonic acid has a strong and agreeable sour taste, like that of tartaric acid; its aqueous solution gives a white precipitate with lead acetate, but does not precipitate the salts of silver, copper, or the metals of the iron group. The *silver*, *calcium*, and *copper salts* are amorphous—the first two white, the third light blue—and have a composition represented by the formula $C^{11}H^{11}M^2O^8$.

Constitution of Cinchonine and its Acid Derivatives.—Weidel attributes to cinchonine the formula—



This would readily give by oxidation $C^9H^8N.CO^2H$, this formula being half that above attributed to cinchoninic acid. The doubling of the formula is justified by the fact that cinchoninic acid splits up sharply into quinolic acid, and cinchomeronic acid (p. 483), and yields acid salts.

Quinolic acid is probably dihydroxyl-nitroquinoline, $C^8H^4N(OH)^2(NO^2)$, as it yields nitrite of potassium on fusion with caustic potash, and is converted by tin and hydrochloric acid into a resinous, easily decomposed amido-product.

Cinchomeronic acid is probably $C^8H^4N^2(CO.OH)^2$.

Oxycinchomeronic acid, $C^8H^4N^2 \begin{Bmatrix} (OH)^2 \\ (CO.OH)^2 \end{Bmatrix}$.

Cinchonic acid, $C^8H^4 \begin{Bmatrix} (OH)^2 \\ (CO.OH)^2 \end{Bmatrix}$.

whilst pyro-cinchonic acid is $C^8H^4 \begin{Bmatrix} OH \\ (CO.OH)^2 \end{Bmatrix}$ bearing to cinchonic acid the same relationship as itaconic acid to citric acid.

Cinchonidine, $C^{20}H^{24}N^2O$ (the quinidine of Henry a. Delondre; α -quinidine of Kerner), crystallises from alcohol in anhydrous needles, prisms, or plates, gives no fluorescence (when pure), and no green coloration with chlorine and ammonia. It is levorotatory. The hydrochloride is $C^{20}H^{24}N^2O.HCl + H^2O$; the sulphate $C^{20}H^{24}N^2O.H^2SO^4 + 6H^2O$ (Hesse).

Sulphato-periodides.— $12C^{20}H^{24}N^2O.9H^2SO^4.8HI.I^{14} + H^2O$, Herapath's brass-yellow salt, is easily prepared by slowly cooling a solution of the theoretical quantities of its constituents in hot alcohol. It crystallises in very fine rhombic golden plates. Bisulphide of carbon is only faintly coloured by it even when hot: ether and chloroform not at all. With mercury it gives mercurous iodide, and a double iodide. It is soluble in hot alcohol.

$4C^{20}H^{24}N^2O.2H^2SO^4.3HI.I^3 + 4H^2O$ almost always separates from the mother-liquor of the previous and following compounds in long, thin, silky, reddish yellow or golden-yellow needles. When pure it loses all its water on drying over sulphuric acid. It imparts no colour to ether, chloroform, or bisulphide of carbon, but is soluble in hot alcohol. The solution does not form mercurous iodide when shaken up with mercury, but an almost white double salt crystallises out on cooling in silky, faintly yellow, stellate masses of flat needles. On dissolving it at a gentle heat in alcohol, with addition of a very little sulphuric acid, a yellowish salt separates out on cooling, and afterwards an olive-green compound into which the whole is finally converted.

$8C^{20}H^{24}N^2O.5H^2SO^4.6HI.I^{12} + 6H^2O$ may be prepared by dissolving 3.08 grams of cinchonidine in 100 c.c. of alcohol (93 per cent.) and adding 10 c.c. of sulphuric acid and 10 of hydriodic acid. If 1.905 grams of iodine in 50 c.c. of alcohol be then added, and the temperature kept at 55° , thin olive-green needles are formed, which must be filtered off before the liquid has cooled to below 30° . This periodide is not the same as the green compound described by Herapath. It has no effect on ether, chloroform, or bisulphide of carbon; it gives a double iodide with mercury, but no mercurous iodide is formed.

$2C^{20}H^{24}N^2O.8H^2O.HI.I^4.H^2O$ is obtained by cooling a solution containing the calculated quantities of the constituents in hot alcohol. It consists of reddish or dark brown stellate masses of short, thick, brilliant needles. It gives no colour to ether, chloroform, or bisulphide of carbon. With mercury it forms mercurous iodide and a double iodide. It is easily convertible by addition of hydriodic acid and dilution with water, into the second compound. Heated to 100° , and boiled with alcohol, it yields for the most part olive-green needles of the third compound (Jørgensen, *J. pr. Chem.* [2], xiv. 387).

Thiocyanate, $C^{20}H^{24}N^2O.HCNS$.—This salt is formed by adding potassium thiocyanate to a warm aqueous solution of the sulphate or hydrochloride, a milky turbidity being first produced, and the thiocyanate soon after separating in slender white anhydrous prisms. It dissolves in 205 pts. of water at 20° , easily in boiling water and in alcohol, is nearly insoluble in ether, and quite insoluble in solution of potassium thiocyanate. An aqueous solution of phenol added to the aqueous solution of this salt produces a milky turbidity and afterwards an oily precipitate, above which colourless prisms gradually form.

The neutral salt treated with sulphuric acid is converted into an oily acid salt (Hesse, *Liebig's Annalen*, clxxxi. 50).

Phenol-cinchonidine, $C^{20}H^{24}N^2O.C^6H^5O$, is formed by dissolving equivalent quantities of cinchonidine and phenol in hot dilute alcohol, and separates from the solution as an oil which solidifies after a while in beautiful prisms having a glassy lustre. It gives a dark yellow colour with ferric chloride, showing that the phenol reaction in it is masked; the phenol may, however, be separated from it by dilute acids, also by repeated crystallisation from alcohol, and by heating to 120° (Hesse, *Liebig's Annalen*, clxxxi. 53; clxxxii. 160).

Phenol-cinchonidine sulphate, $2C^{20}H^{24}N^2O.SO^2.C^6H^5O + 5H^2O$.—This salt is formed by adding phenol-water (1 : 25) to a hot aqueous solution of neutral cinchonidine sulphate, and separates on cooling in crystals which may be purified by recrystallisation from boiling water. It then forms white shining scentless prisms having the composition $2C^{20}H^{24}N^2O.SO^2.C^6H^5O + 5H^2O$. It dissolves in 425 pts. of water at 15° , easily in boiling water, and is in great part precipitated from a cold saturated aqueous solution by phenol-water. It is readily soluble in hot alcohol, and partly separates in prisms on cooling. Ferric chloride produces with it a dark yellow colour, showing that the phenol is not thereby separated; a separation of phenol takes place however when the solution of the salt is treated with dilute acids or with ammonia or other bases.

Phenol-cinchonidine hydrochloride, $2C^{20}H^{24}N^2O.HCl.C^6H^5O$, is formed by dissolving cinchonidine hydrochloride and phenol in equivalent proportions in hot water, and separates on cooling in crystals which may be purified by recrystallisation from boil-

ing water. It forms white granular crystals containing 1 mol. H_2O . Heated to 100° in an open crucible, it gives off water together with considerable quantities of phenol, and a further quantity (about 22 per cent. in all) at 120° , turning brown at the same time and dissolving with brown colour in water. But when heated to about 100° in a loosely closed test-tube, it melts and gives off water, and the mass, if then left to cool, becomes covered with a crystalline crust, while the interior remains fluid for a long time, this fluid mass evidently consisting of the anhydrous salt. Partial fusion likewise takes place when the crystallised substance is heated with hot water.

The salt dissolves easily in alcohol and in hot water, in 46 pts. of water at 15° , and is partially precipitated from the last-mentioned solution by phenol-water. It dissolves easily in chloroform, very sparingly in ether. Its specific rotatory power at 15° for the D line is -124.12° . With ferric chloride it behaves like the phenol-sulphate; the phenol contained in it has lost its caustic properties, but is easily liberated by acids or alkalis. On adding platinic chloride to a dilute solution of the hydrochloride in phenol-water, a precipitate is formed consisting of the platino-chloride of cinchonidine.

Another phenol-cinchonidine, $2\text{C}^{20}\text{H}^{24}\text{N}^2\text{O} \cdot 3\text{C}^6\text{H}_6\text{O}$, is formed when 1 mol. cinchonidine and 2, 3, or more molecules of phenol are dissolved together in alcohol. It closely resembles the preceding compound, and is likewise decomposed by hot alcohol; a solution of 1 pt. of the compound in 5 pts. alcohol, first depositing crystals of $2\text{C}^{20}\text{H}^{24}\text{N}^2\text{O} \cdot \text{C}^6\text{H}_6\text{O}$, and on further recrystallisation, pure cinchonidine.

Chlorocinchonidide, $\text{C}^{20}\text{H}^{24}\text{N}^2\text{Cl}$. This compound is formed, like the corresponding cinchonine derivative (p. 482), by heating cinchonidine to 140° – 150° with highly concentrated hydrochloric acid.

The contents of the tube may be diluted with water without separation of crystals, and ammonia added to the solution throws down the chlorocinchonidide as a white bulky precipitate, which dissolves in alcohol, and separates from the solution in brightly nacreous scales having the composition $\text{C}^{20}\text{H}^{24}\text{N}^2\text{Cl} + \text{H}_2\text{O}$ (Zorn, *J. pr. Chem.* [2], viii. 279).

Dioxycinchonidine, $\text{C}^{20}\text{H}^{22}\text{N}^2\text{O}^2$. When bromine is added to a mixture of finely powdered cinchonidine and carbon sulphide, the compound, $\text{C}^{20}\text{H}^{22}\text{BrN}^2\text{O} + 2\text{HBr}$, is obtained in fine yellow needles. It is insoluble in carbon sulphide, but dissolves in alcohol. When this solution is boiled with water to remove the alcohol, and the liquid is evaporated in a vacuum, the hydrobromide is obtained in long colourless needles. By the continued action of boiling alcoholic potash, this salt is converted into *dioxycinchonidine*, $\text{C}^{20}\text{H}^{22}\text{N}^2\text{O}^2$, forming ramified crystals. The normal sulphate of this base, $(\text{C}^{20}\text{H}^{22}\text{N}^2\text{O}^2) \cdot \text{SO}_4\text{H}^2 \cdot 2\text{H}_2\text{O}$, forms strongly refractive white plates. On dissolving it in dilute sulphuric acid and evaporating the solution over oil of vitriol, the acid salt, $\text{C}^{20}\text{H}^{22}\text{N}^2\text{O}^2 \cdot \text{SO}_4\text{H}^2$, is obtained in hard crystals. The platinum salt, $\text{C}^{20}\text{H}^{22}\text{N}^2\text{O}^2 \cdot 2\text{HCl} \cdot \text{PtCl}_4$, is a crystalline precipitate insoluble in water. Dioxycinchonidine has the same composition as oxyquinine, which Schützenberger obtained by boiling quinine sulphate with potassium nitrite (iv. 320), but does not appear to be identical therewith (Skalweit, *Liebig's Annalen*, clxxii. 102).

Cinchonidine, $\text{C}^{20}\text{H}^{24}\text{N}^2\text{O}$, is prepared, similarly to quinine, by the action of heat on the acid sulphate of cinchonine or cinchonidine. This salt, after drying in the exsiccator, melts at 130° , and is converted into cinchonidine bisulphate without the slightest alteration of weight. Cinchonidine may also be prepared from cinchonine, but not so conveniently, as the bisulphate of that base does not crystallise readily. The melted mass is dissolved in water, the solution supersaturated with ammonia and shaken up with ether, the ether evaporated in the exsiccator, and the residue converted into neutral oxalate, which crystallises after a while, and is to be dried in the exsiccator, freed from colouring matters by repeated crystallisation from boiling chloroform, and finally recrystallised from water.

To obtain the cinchonidine from this salt, it is mixed with slaked lime or caustic soda and a little water, and the separated alkaloid is taken up with absolute ether. On evaporating the colourless ethereal solution, the cinchonidine remains as a slightly yellowish amorphous mass, which, when dried in the same manner as quinine, first in the exsiccator, and then in a vacuum at 62° , gives by analysis numbers which show that it is isomeric with cinchonine and cinchonidine, and does not form a hydrate.

Cinchonidine forms a slightly yellow viscous mass which may be drawn out into colourless threads. It melts to a mobile liquid at about 50° , becomes brown at about 80° , and at 100° or above is converted into a dark-brown mass of the colour of quinaidine. It dissolves easily in alcohol, ether, chloroform, acetone, and benzene. Its alcoholic solution has a bitter taste and strong basic reaction, and neutralises acids completely.

Cinchonicine is not coloured by chlorine and ammonia. Its hydrochloric acid in solution gives with chloride of lime or Labarraque's reagent, a white flocculent precipitate not coloured by ammonia; this reaction distinguishes it from cinchonine and cinchonidine, which give no precipitate with Labarraque's solution. It is decomposed by heating with strong nitric acid, not perceptibly by aqueous sulphuric acid (1 : 4). Its solution in sulphuric acid reduces potassium permanganate at least as quickly as cinchonine; the product of the reaction is not, however, cinchotenine, but a resinous substance probably identical with Marchand's cinchonetine.

Cinchonicine is more soluble in water than quinine. Its aqueous solution reacts with soda and with ammonia in the same manner as quinine.

With phenol cinchonicine behaves like cinchonine and quinidine, forming an oily compound easily soluble in water and imperfectly precipitated from the solution by phenol-water.

Cinchonicine salts. The neutral oxalate crystallises from chloroform or from water in small delicate white prisms, often interlaced and bearing a strong resemblance to fungus-threads (mycelia). It dissolves very easily in alcohol, boiling chloroform, and boiling water, sparingly in cold chloroform, and in 80 pts. of water at 60°. The hot aqueous solution remains supersaturated for a long time after cooling. It dissolves readily also in a mixture of alcohol and chloroform. It gives off part of its water of crystallisation at ordinary temperatures in the exsiccator, and the rest at 100°, the total quantity given off agreeing with the formula $2C^{20}H^{24}N^2O \cdot C^2H^2O^4 + 4H^2O$. According to Howard it contains $7H^2O$, but Hesse has found 4 mols. water also in a specimen of the salt prepared by Howard.

The hydriodide, $C^{20}H^{24}N^2O \cdot HI$, obtained by precipitating a solution of the oxalate with potassium iodide, separates as a white anhydrous crystalline powder, afterwards turning yellow, and consisting of short thick prisms, moderately soluble in cold, easily in hot water, very easily in boiling alcohol, and separating therefrom on cooling in fine prisms; very sparingly soluble in solution of potassium iodide.

The platinochloride, $3C^{20}H^{24}N^2O \cdot HCl \cdot 2PtCl^4 + 4H^2O$, separates on adding platonic chloride to a cold slightly acid solution of cinchonicine hydrochloride, as a white precipitate which gradually changes to a light yellow crystalline powder. In a warm solution platonic chloride first produces a milky turbidity, followed by separation of the platinum salt in flocks. The aurochloride separates as a yellow oily precipitate from a mixture of the hydrochloride with auric chloride. The mercuriochloride is also an oily precipitate, soluble in hydrochloric acid and in water, but apparently uncrystallisable.

Thiocyanate.—Potassium thiocyanate, added to cinchonicine hydrochloride, produces only a milky turbidity which disappears on further addition of the potassium thiocyanate.

Behaviour of the Solutions of Cinchonicine and Quinine to Polarised Light.—Cinchonicine and quinine turn the plane of polarisation to the right, but less strongly than cinchonine and quinidine. Pasteur is of opinion that the last-named bases contain two optically active atomic groups, one of which is feebly, the other strongly dextrogyrate, and that in quinine and cinchonidine the latter group is replaced by another which is levogyrate. The first action of heat is to alter the relative positions of the atoms in these groups, in such a manner as to render them optically inactive, in consequence of which the newly-formed molecule turns the plane of polarisation only slightly to the right or to the left. Howard (*Chem. Soc. J.* [2], xi. 1177) from a review of determinations made by Hesse and others, and from his own observations on the ethyl-derivatives of the several bases, infers that the rotatory powers of quinine and cinchonicine are very nearly equal to the arithmetical means of the rotatory powers of quinine and quinidine, and of cinchonine and cinchonidine respectively. To test the validity of this view, Hesse (*Liebig's Annalen*, clxxviii. 260) has made a number of observations on the rotatory power of the several bases, the results of which are given in the following table. The temperature of experiment was in all cases 15° C.; the angles of rotation relate to the Fraunhofer line D:—

Quinicine	+ 21.83°	} ar. mean = + 21.88
Quinine	— 278.81°	
Quinidine	+ 322.58°	
Cinchonicine	32.52°	} ar. mean = + 41.7
Cinchonine	+ 258.78°	
Cinchonidine	— 175.38°	

From these results it appears that the actual rotatory powers of quinine and cinchonicine differ considerably from the arithmetical means of those of the original substances.

Acetyl-cinchoninicine, $C^{10}H^{22}(C^2H^3O)N^2O$, formed, like the corresponding quinine compound (p. 486), by heating cinchonine or cinchonidine with acetic anhydride, is obtainable only as a varnish, and does not form crystalline salts. By saponification it yields cinchoninicine somewhat impure, but having the rotatory power of the ordinary base.

HOMOCINCHONINE GROUP.

c, $C^{10}H^{22}N^2O$, the 'cinchonidine' of Koch (*Pharmac. Post*, x. 207 [1877]), is one of the constituents of the bark of *Cinchona rosulenta*. It crystallises from alcohol in large prisms and small plates. Laevo-rotatory. A solution of 2 grams in 100 c.c. of 97 per cent. alcohol at 15° , gives the value—

$$(\alpha)_D = -109.34^\circ.$$

The hydrochloride is $C^{10}H^{22}N^2O.HCl.H^2O$, and the sulphate $(C^{10}H^{22}N^2O)^2.H^2SO^4.6H^2O$. This alkaloid has been mistaken for aricine, owing to the circumstance that its sulphate, under certain conditions, separates as an amorphous mass, instead of forming slender needles.

Homocinchoninicine, $C^{10}H^{22}N^2O$, is derived from homocinchonidine, just as cinchoninicine and quinicine are derived from their respective isomerides, by heating the sulphates, &c. Amorphous, but forms a crystalline oxalate, $(C^{10}H^{22}N^2O)^2.C^2H^2O^4.4H^2O$, remarkably like that of cinchoninicine.

Dihomocinchoninicine (Hesse's dihomocinchonine), $C^{20}H^{44}N^4O^2$, accompanies the homocinchonine alkaloids in *C. rosulenta*. Strongly dextro-rotatory. Amorphous; yields only amorphous salts (Hesse).

QUININE GROUP.

Quinine, $C^{20}H^{24}N^2O^2$. *Physical properties of Quinine and its salts*.—The solubility of quinine in water is 1 in 2024 pts. at 15° ; in absolute alcohol, 1 in 1.133 pts. at 15° ; in chloroform, 1 in 1.926 pts. at 15° ; and in pure ether, 1 in 22.632 pts. at 15° .

The solubility of quinine tannate in water at 15° is less than 1 in 20,000 pts.

The fluorescent properties of quinine sulphate become 25 times more marked in presence of excess of sulphuric acid. Owing to this increased fluorescence, it is possible to recognise the presence of quinine in a solution containing $\frac{1}{100,000}$ of its weight of the alkaloid. This test surpasses that of turbidity caused by Nessler's reagent, in the proportion of 5 : 4; the latter test, moreover, gives no indication of the nature of the alkaloid (*J. Regnaud, J. Pharm. Chim.* [4], xxi. 8). See also Prescott, *Pharm. J. Trans.* [3], viii. 407; *Chem. Soc. J.* 1877, ii. 933).

According to Hesse (*Deut. Chem. Ges. Ber.* x. 2152), crystallised anhydrous quinine melts at 177° , and dissolves in 19.60 pts. water at 15° ; the trihydrate melts at 57° and dissolves in 1670 pts. water at 15° .

Deazotisation.—According to J. D. Boeke (*Deut. Chem. Ges. Ber.* vi. 488), quinine distilled with zinc and zinc-sodium yields a distillate free from nitrogen and smelling like cumia oil, and a residue containing sodium cyanide.

Reaction with Hydrochloric acid.—Quinine heated to 140° – 150° for several hours with very concentrated hydrochloric acid, is decomposed in the same manner as cinchonine (p. 482), a solution being formed which, when evaporated, yields a beautifully crystalline compound, $C^{20}H^{22}ClN^2O.2HCl.H^2O$, the hydrochloride of chloroquinide. Its solution is not fluorescent, and is not coloured green by chlorine-water and ammonia.

Only one of the two oxygen-atoms of quinine can be removed by this reaction, and this renders it probable that quinine contains only one hydroxyl-group. It is therefore impossible to obtain a base identical with quinine by the action of alcoholic potash on monochlorocinchonine. The oxycinchonine obtained by this process is, in fact, isomeric, not identical with quinine (*W. Zorn, J. pr. Chem.* [2], viii. 279).

Sulphates. According to A. J. Cowley (*Pharm. J. Trans.* [3], vii. 189), perfectly uneffloresced neutral quinine sulphate has the composition $(C^{20}H^{24}N^2O^2)^2.H^2SO^4 + 7\frac{1}{2}H^2O$, and gives off the whole of its water at 100° , but recovers 2 mol. on exposure to the air. The effloresced salt also contains $2H^2O$. According to Hesse (*loc. cit.*), the neutral salt crystallises with $8H^2O$, the acid salt, $C^{20}H^{22}N^2O^2.H^2SO^4$, with $7H^2O$.

Periodides. A solution of acid quinine sulphate mixed with a solution of iodine in potassium iodide, yields a kermes-brown precipitate consisting of a diiodide, $C^{20}H^{24}N^2O^2.HI^2$, which crystallises from alcohol in bronze-coloured laminae, is decomposed by water, dissolves in nitric acid with transient red colour, and is

soluble in potassium iodide solution, ether, chloroform, and benzene. If alcoholic solutions are used, another di-iodide is obtained, soluble in water, but insoluble in benzene and in chloroform. The pent-iodide, $C^{20}H^{21}N^2O^2.HI^5$, is produced when a solution of the di-iodide is mixed with excess of iodine, and separates in nearly black prisms, contaminated with a resinous body which cannot be completely removed. When 2 pts. of quinine are triturated with 1 pt. of iodine, the product treated with alcohol, and the solution left to evaporate, there is obtained a brown resinous product insoluble in alcohol, and consisting, not of $(C^{20}H^{21}N^2O^2)I^2$, as stated by Pelletier, but of $(C^{20}H^{21}N^2O^2)I^3$, together with a compound, $(C^{20}H^{21}N^2O^2)I^4$, which is soluble in alcohol, and is separated therefrom by water as a yellow amorphous precipitate (H. R. Bauer, *Arch. Pharm.* [3], v. 214; *Jahrb. f. Chem.* 1874, 860).

Sulphatoperiodides (Jørgensen, *J. pr. Chem.* [2], xiv. 213). Quinine forms many compounds similar to herapathite, and they may be divided into two series. One, to which herapathite proper belongs, contains 3 mols. of sulphuric acid to 4 of quinine; the other, 1 mol. of acid to 2 of quinine. The first series consists of tolerably stable compounds, while the salts of the other series are prone to decomposition, with formation of compounds belonging to the first series.

(1.) *Herapathite*, $4C^{20}H^{21}N^2O^2.3H^2SO^4.2HI.I^4 + xH^2O$, is best prepared by dissolving neutral quinine sulphate in the calculated quantity of sulphuric acid, warming with alcohol up to boiling, mixing with the calculated quantity of hydriodic acid and iodine, the first in aqueous, the second in alcoholic solution, and allowing the whole to cool slowly. It contains unaltered quinine, and one-third of the iodine is present as hydriodic acid.

(2.) $8C^{20}H^{21}N^2O^2.6H^2SO^4.4HI.I^6$.—There are several methods of obtaining this compound. One is to dissolve one molecule of neutral quinine sulphate with two molecules of sulphuric acid in alcohol, and to add to the solution heated to boiling one atom of iodine dissolved in alcohol. The crystals of this salt have a metallic lustre, and are of an olive-gray colour, between the grass-green of herapathite and the bronze-yellow of the next compound. They are more soluble in warm than in cold alcohol, but not so soluble as herapathite.

(3.) $4C^{20}H^{21}N^2O^2.3H^2SO^4.2HI.I^4 + 2H^2O$ may be formed by addition of 1 pt. of iodine to $3\frac{1}{2}$ pts. of herapathite in alcoholic solution. It crystallises in long flat needles or in plates of the same form as herapathite. It is of a bronze-yellow colour, and is less soluble than herapathite in hot alcohol. On recrystallisation it is decomposed into iodine and the previous compound.

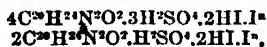
(4.) $8C^{20}H^{21}N^2O^2.6H^2SO^4.4HI.I^4 + 4H^2O$.—Formed in the attempt to produce the 7th compound (see below) from the calculated quantities of quinine sulphate, hydriodic acid, and iodine. Bronze-yellow brownish needles with fine metallic lustre. It is isomorphous with the previous compound.

(5.) $2C^{20}H^{21}N^2O^2.H^2SO^4.2HI.I^2$.—Obtained by mixing an almost cold solution of 1 mol. of neutral quinine sulphate in alcohol, with two atoms of iodine dissolved in hot alcohol, and allowing the mixture to stand for two hours. It consists of long, red, brilliant needles, which in air become changed into a black glassy mass.

(6.) $2C^{20}H^{21}N^2O^2.H^2SO^4.2HI.I^4$.—The calculated quantities of neutral quinine sulphate, hydriodic acid and iodine are dissolved in hot alcohol, and the solution is mixed with so much hydriodic acid that nothing crystallises out on cooling. On cautious addition of water, olive-green laminae separate. This compound is more soluble in hot than in cold alcohol, but cannot be crystallised from this solvent. Herapathite is deposited on cooling.

(7.) $2C^{20}H^{21}N^2O^2.H^2SO^4.2HI.I^6$ may be obtained in several ways—for instance, by mixing a hot alcoholic solution of herapathite with a large quantity of solution of iodine, diluting somewhat with water, and allowing the mixture to stand. This compound forms brilliant black needles and laminae with a greenish reflection. If washed with too strong a solution of alcohol, the crystals resemble potassium permanganate in appearance. They cannot be recrystallised, for although they dissolve slowly in alcohol, another compound, not yet accurately examined, separates on cooling.

In addition to the two classes of salts above described—



a third seems to exist, of the composition $3C^{20}H^{21}N^2O^2.2H^2SO^4.2HI.I^4$. The salts of this series have not yet been examined with sufficient accuracy to settle their formulae with certainty, but the results hitherto obtained are as follows:—

(a.) $3C^{20}H^{21}N^2O^2.2H^2SO^4.2HI.I^2$ (?).—This compound consists of groups of fine

needles which are blue by transmitted light when in thin layers. It is obtained during the recrystallisation of the next substance.

(β .) $3C^{10}H^{19}N^2O^2.2H^2SO^4.2HI.I^*$ (?).—Consists of olive-grey laminæ, which separate from a hot alcoholic solution of acid sulphate of quinine on addition of varying quantities of solution of iodine.

(γ .) $3C^{10}H^{19}N^2O^2.2H^2SO^4.2HI.I^*$ (?).—Obtained only once in a pure state from one molecule of neutral sulphate of quinine, 2 mols. of normal sulphuric acid, and 200 c.c. of an old solution of iodine containing 16.8 grams of free iodine. All attempts to reproduce this body with a freshly prepared solution of iodine failed. It consists of olive-green needles with metallic lustre, which polarise light in exactly the opposite direction to herapathite.

SULPHATO-PERIODIDES OF METHYL-QUININE.—(1.) $2C^{10}H^{19}N^2O^2(CH^3).I.H^2SO^4.I^*$. This compound is obtained by slowly cooling a mixture of the theoretical quantities of methyl-quinine iodide and sulphuric acid, with about four-fifths of the calculated quantity of iodine in alcoholic solution at a temperature of about 60° . It consists of reddish-brown needles, often several centimeters long, which are easily soluble in hot alcohol.

(2.) $2C^{10}H^{19}N^2O^2(CH^3).I.H^2SO^4.I^*$.—Most easily prepared by slowly cooling a mixture of methyl-quinine iodide, sulphuric acid, and iodine (in the calculated quantities) from a hot alcoholic solution. It consists of very fine brilliant brown laminæ, soluble with difficulty even in hot alcohol.

(3.) $4C^{10}H^{19}N^2O^2(CH^3).I.2H^2SO^4.I^*$.—Prepared by warming an alcoholic solution of No. 1 to 60° , and adding an alcoholic solution of four atoms of iodine of the same temperature. It consists of brilliant, almost black laminæ, which must be filtered off from the still warm solution and washed with alcohol at about 80° . The temperature must be kept down, or else the product consists chiefly of No. 2. It dissolves with difficulty in hot alcohol.

(4.) $4C^{10}H^{19}N^2O^2(CH^3).I.2H^2SO^4.I^*$.—Obtained by mixing a hot alcoholic solution of No. 1 with a large excess of a cold solution of iodine. It consists of long, thin, almost black needles, with a greenish metallic lustre. The crystals dissolve with difficulty in hot alcohol.

Compounds containing 4 mols. of methyl-quinine to 3 of sulphuric acid have not been obtained.

SULPHATOPERIODIDE OF QUININE-METHYLQUININE.—An attempt was made to prepare herapathite with methyl-quinine hydriodide in place of hydriodic acid, by mixing the calculated quantities of methyl-quinine iodide, quinine sulphate, and iodine, in hot alcoholic solution. The result was a compound of herapathite with No. 1 sulphatoperiodide of methyl-quinine, and water. This body crystallises in dark chocolate-brown masses, which appear under the microscope as carmine-red intertwined hairs. The water is given off at 100° . The compound dissolves with some difficulty in hot alcohol.

Thiocyanates. Quinine treated with thiocyanic acid, forms a neutral and an acid salt, the former being white, the latter yellow (v. 23). The *neutral salt*, $C^{10}H^{19}N^2O^2.HCNS + H^2O$, is also formed when a warm moderately strong aqueous solution of quinine hydrochloride is mixed with potassium thiocyanate, and separates on cooling in slender white needles. It dissolves easily in a mixture of 2 vol. chloroform and 1 vol. absolute alcohol, and exhibits in this solution a specific rotatory power (α)_D = -129.31 . It is completely precipitated from its aqueous solution by small quantities of potassium thiocyanate. When a very large quantity of potassium thiocyanate is added to an aqueous solution of a neutral quinine salt, the quinine thiocyanate separates at first as an oil which afterwards solidifies; but on dissolving the mass in hot water, the salt separates on cooling in white needle-shaped crystals. The aqueous solution of the thiocyanate mixed with aqueous *phenol*, becomes turbid, and gradually deposits dull white prisms of a compound of phenol and quinine thiocyanate (Hesse, *Liebigs Annalen*, *clxxxii.* 48).

On the microscopical appearance of this salt during its formation, see p. 476.

The *acid salt*, $C^{10}H^{19}N^2O^2.2HCNS + \frac{1}{2}H^2O$, separates, on adding dilute sulphuric acid and potassium thiocyanate to a solution of the neutral salt, in long sulphur-yellow needles which gradually change to short compact prisms. At 100° the crystals become opaque, and give off from 1.2 to 1.6 per cent. water of crystallisation (Hesse, *loc. cit.*)

Meconate. Obtained, on mixing the alcoholic solutions of quinine and meconic acid, as a white flocculent precipitate soluble in hot water, and separating on cooling

in fine crystals having the composition $C^7H^2(C^{20}H^{21}N^2O^2)O'$ (P. T. Austen, *Pharm. J. Trans.* [3], iii. 1016).

Salicylate, $C^{20}H^{21}N^2O^2.C^7H^4O^2$.—Separates on adding a solution of quinine hydrochloride in cold water, to ammonium salicylate as a curdy precipitate, which crystallises from alcohol in concentric groups of anhydrous prisms (Jobst).

Phenate, $C^{20}H^{21}N^2O^2.C^6H^4O$. Separates from water and from alcohol in delicate needle-shaped crystals (Jobst, *N. Rep. Pharm.* xxiv. 193).

Compounds of Phenol with Neutral Quinine Salts (Jobst & Hesse, *Liebig's Annalen*, clxxx. 248). 1. With the neutral sulphate, $2C^{20}H^{21}N^2O^2.SO^2.C^6H^4O + 2H^2O$. This compound, which may be regarded as *phenol-sulphate of quinine*, is formed by mixing a hot aqueous solution of the sulphate with an equivalent quantity of phenol, and separates in crystals on cooling; also by dissolving quinine sulphate in a hot alcoholic solution of phenol. It may be purified by one crystallisation from hot alcohol, and then forms white shining prisms, easily soluble in boiling water and alcohol, soluble at 15° in 680 pts. of water, and 74 pts. of 80 per cent. alcohol. Ether and pure chloroform dissolve only traces of it, but a mixture of 2 vol. chloroform and 1 vol. absolute alcohol dissolves it readily. In the latter solution at 15° its specific rotatory power is $(\alpha)_D = -158.83$.

Quinine phenolsulphate gives with ferric chloride in aqueous or alcoholic solution, a yellowish coloration; with moderately strong nitric acid a brown-red solution, from which, after dilution with water, ammonia added in excess throws down a yellow precipitate. At 100° it gives off nothing but water of crystallisation, but at 130° and above, small quantities of phenol are given off, and the compound undergoes further decomposition.

2. With the hydrochloride, $2(C^{20}H^{21}N^2O^2.HCl).C^6H^4O + 2H^2O$.—This compound, which may be called *phenol-hydrochloride of quinine*, crystallises on cooling from a hot aqueous solution of quinine hydrochloride mixed with phenol, in white prisms, which may be completely purified by once recrystallising them from boiling water. It dissolves easily in hot water and in alcohol, in 101 pts. water at 15° , in 4 pts. alcohol of 80 v. per cent.; other dissolves only traces of it. In its solution in alcohol of 97 vol. per cent. at 15° , its specific rotatory power is $(\alpha)_D = 140.45^\circ$.

This salt has a bitter taste, not much like that of phenol. Both acids and bases set the phenol free. It gives a brownish-yellow colour with ferric chloride. It gives off its water of crystallisation at 100° , and phenol with partial fusion at 120° .

The same compound is formed by decomposing the phenolsulphate of quinine with barium chloride, and in a similar manner other salts may be formed, e.g. the *phenol-hydrobromide*, which crystallises in white prisms.

Quinidine or Conchinine, $C^{20}H^{21}N^2O^2$, crystallises from alcohol in prisms with $2\frac{1}{2}H^2O$; from ether in rhombohedrons with $2H^2O$; from boiling water in thin plates containing $1\frac{1}{2}H^2O$; neither of the last two kinds of crystals effloresce in the air (Hesse). Quinidine treated with strong hydrochloric acid in the manner described for cinchonine and quinine, yields a similar chlorinated product, which separates from the contents of the tube diluted with half their bulk of water, in large shining prisms resembling chloride of cinchonidine, but differing from that compound by giving a green colour with chlorine-water and ammonia. Ammonia added to the aqueous solution, throws down the chlorinated base. Its composition could not be exactly determined, but it appears to have the composition, $C^{20}H^{21}N^2OCl + HCl$, the base being formed, as in the case of the corresponding cinchonine and quinine-derivatives, by the substitution of 1 at. Cl for 1HO in quinidine (Zorn, *J. pr. Chem.* [2], viii. 279).

Quinidine Sulphate. The purity of this salt may be tested by adding 1 pt. of potassium iodide to 1 pt. of the sulphate dissolved in 20 pts. of water at 60° , and filtering from the precipitate after the lapse of an hour. The clear solution thus obtained should give no turbidity with ammonia, as this would indicate the presence of quinine, cinchonine or cinchonidine. Another mode of testing is to add 6 pts. of Rochelle salt to 1 pt. of the sulphate dissolved in 80 pts. of water at 60° ; if a precipitate be thereby formed, the presence of quinine or cinchonidine may be inferred. If ammonia be then added to the filtrate, a precipitate of quinidine hydriodide will be formed, and the filtrate from this may be tested with ammonia for cinchonine as above. The presence of calcium or sodium salts may be detected by treating the salt with a mixture of 2 vol. chloroform and 1 vol. alcohol of 97 per cent., which will dissolve the quinidine salt, and leave the inorganic salts undissolved (Hesse, *Liebig's Annalen*, clxxvi. 326).

Neutral quinidine sulphate crystallises with $2H^2O$, the acid sulphate with $4H^2O$; the hydrochloride with $1H^2O$ (Hesse).

Thiocyanates. The neutral salt, $C^{20}H^{14}N^2O^2.HONS$, separates on adding potassium thiocyanate to the concentrated solution of an easily soluble neutral quinidine salt, as an oily precipitate quickly converted into small crystals. From warm and somewhat dilute solutions on the other hand, the salt immediately separates in the form of a white crystalline powder, and from very dilute solutions in distinct prisms. It is anhydrous, dissolves in 1477 pts. of water at 20° , rather sparingly also in boiling water, from which it separates on cooling in small prisms. From boiling alcohol, in which it is very slightly soluble, it crystallises on cooling in large white prisms (Hesse, *Liebig's Annalen*, clxxxi. 51).

On the microscopical characters of this salt, see p. 476.

The acid salt, $C^{20}H^{14}N^2O^2.2HCNS + H^2O$, is formed by dissolving the neutral salt, together with potassium thiocyanate, in warm dilute sulphuric acid, and separates on cooling in long sulphur-yellow many-faced prisms, which gradually change to shorter prisms of the same colour. These crystals dissolve partially in boiling water, while the undissolved portion melts. The aqueous solution then becomes milky on cooling, and exhibits a strong acid reaction, but no fluorescence (Hesse).

Phenol-compounds. Quinidine salts, like those of quinine, unite with phenol, but the resulting compounds are amorphous, oily, and easily soluble in cold water. They are precipitated from their aqueous solutions by an excess of phenol-water (Hesse).

Sulphatoperiodides (Jørgensen, *J. pr. Chem.* [2], xiv. 356). $2C^{20}H^{14}N^2O^2.H^2SO^4.2HI.I^2$, prepared by dissolving quinidine in the calculated quantity of strong sulphuric acid and hot alcohol, and adding the calculated quantity of hydriodic acid, and a little less than the required quantity of iodine in hot alcoholic solution, crystallises in red needles with a bluish lustre, which scarcely absorb polarised light, and are very brilliant. After being heated to 100° they decoloritate strongly on cooling, showing that they are anhydrous.

$3C^{20}H^{14}N^2O^2.3H^2SO^4.2HI.I^2$ is best obtained by dissolving 35 grams of quinidine (containing 8–10 per cent. water) in 25 c.c. dilute sulphuric acid (17 per cent. SO^4), and 60 c.c. alcohol (92 per cent.), and adding 2 grams of iodine dissolved in 60 c.c. of the same spirit. The iodine-solution must not be heated above 50° , and the acid liquid should not have a much higher temperature. This compound forms olive-brown plates or flattened prisms. It undergoes a gradual spontaneous change, the amount of free iodine diminishing, though the total amount of that element remains unaltered. It easily passes into the preceding compound. It dissolves in hot alcohol, and the solution on cooling deposits a reddish-brown powder, together with shining brown prisms, very much like the preceding sulphatoperiodide, but having a different composition.

Ethyl-quinidium-compounds. The iodide, $C^{20}H^{14}N^2O^2.C^2H^5.I$, is deposited in colourless silky needles, on mixing an alcoholic solution of quinidine with ethyl-iodide and excess of ether. A solution of the neutral chloride may be obtained by digesting the iodide with silver chloride and water; it is not precipitated by caustic soda or ammonia, or by alkaline carbonates. It gives an orange-coloured precipitate with platonic chloride, yellow with gold chloride, white with potassio-mercuric iodide. The tri-iodide, formed on adding a solution of potassium periodide to a hot alcoholic solution of the chloride, crystallises in long brown needles.

The sulphato-periodide, $2C^{20}H^{14}N^2O^2.C^2H^5.I.H^2SO^4.I^2$, is formed on mixing 2 mol. ethyl-quinidium iodide and 1 mol. sulphuric acid with hot alcohol of 93 per cent., and adding 4 mol. iodine dissolved in hot alcohol, and crystallises on cooling in dark brown prisms having a metallic lustre, and slightly soluble in hot alcohol. It does not colour chloroform, ether, or carbon sulphide (Jørgensen).

Quinicine. $C^{20}H^{14}N^2O^2$ (Hesse, *Liebig's Annalen*, clxxviii. 244; *Deut. Chem. Ges. Ber.* x. 2152). 1. This base, isomeric with quinine and quinidine, is prepared by heating the finely pounded acid sulphate of quinine or quinidine to 136° , the conversion of about 5 grams of the salt into the isomeric quinicine sulphate being completed in a few minutes. For purification the aqueous solution of the salt is either neutralised with ammonia, and after a few days, is recrystallised; or monia, shaken up with ether, and the base thus liberated is converted into neutral oxalate, which is crystallised from boiling chloroform, and afterwards from alcohol of 97 per cent. On again precipitating with ammonia, dissolving the precipitate in ether, washing the ethereal solution with water, and leaving the ether to evaporate, the quinicine remains as a slightly yellowish amorphous mass, which obstinately re-

tains ether and water. When dried at 62° under a pressure of 430 mm., it gave by analysis numbers agreeing exactly with the formula $C^{20}H^{24}N^2O^7$.

Quinicine melts at about 60° , acquiring at the same time a red-brown colour; at 100° – 110° this change of colour takes place more quickly, but still without loss of weight; at 130° – 140° it assumes the appearance of quinoidine, exhibits red spots, and is then no longer easily convertible into the crystallised oxalate.

On the relations of quinicine to *polarised light*,[†] see CINCHONICINA (p. 494).

Quinicine tastes bitter; in alcoholic solutions it exhibits an alkaline reaction, and absorbs carbonic anhydride from the air; its alcoholic solution is coloured green by chlorine-water and excess of ammonia, but less deeply than a similar solution of quinine or cinchonine. It is distinguished from these two bases by yielding in a dilute hydrochloric acid solution a white amorphous precipitate with sodium hypochlorite (Labarraque's solution); chloride of lime also yields a similar precipitate. If the solution be very acid, a precipitation takes place only after a portion of the acid has been neutralised by the reagent; ammonia then colours it yellowish-green. Reaction also takes place in cold nitric acid solution, but if the solution be warmed, red fumes are given off, and no precipitation takes place. The sulphuric acid solution is yellow, and shows no fluorescence.

Quinicine dissolves very easily in alcohol, chloroform, and ether, sparingly in water. If, therefore, an aqueous solution of a quinicine salt be mixed with excess of ammonia or caustic soda, the alkaloïd is precipitated, and collects as an oily mass at the bottom of the vessel. With ammonia, however, the precipitation is never complete, since the ammonia-salt formed at the same time exerts a solvent action on the separated alkaloïd. The quinicine may in either case be dissolved out by ether. This reaction may be employed to separate quinicine from quinoidine and its salts.

With *phenol* quinicine reacts like quinidine, forming an oily compound easily soluble in cold water, and imperfectly precipitated from the solution by phenol-water.

Quinicine salts for the most part crystallise well, but are apt to turn yellow or reddish.

The *acid sulphate* is obtained directly by the action of heat on the corresponding salt of quinine or quinidine, and crystallises gradually from the aqueous solution of the melted mass, in radiate groups of long yellow prisms, very soluble in water.

The *neutral sulphate*, $2C^{20}H^{24}N^2O^7 \cdot SH^2O^4$, crystallises from alcohol of 97 per cent. in delicate reddish-yellow prisms, shrinking up on drying in the air to an amorphous mass which yields a faintly reddish powder. It dissolves very easily in water and in boiling alcohol, and crystallises from the latter on cooling. Pure chloroform dissolves it but sparingly, even at the boiling heat, but alcoholic chloroform dissolves it readily. Its aqueous solution is not precipitated by Rochelle salt. The salt crystallised from alcohol has the composition $2C^{20}H^{24}N^2O^7 \cdot SH^2O^4 + 3H^2O$; the crystals which separate from alcoholic chloroform contain $8H^2O$, but they quickly lose a portion of their water on exposure to the air.

The *neutral oxalate*, $2C^{20}H^{24}N^2O^7 \cdot C^2H^2O^4 + 9H^2O$, crystallises from hot chloroform in small white prisms; from a hot saturated alcoholic solution in long faintly yellowish, very light needles; from water it appears to separate only in yellowish prisms. It dissolves easily in boiling, sparingly in cold water, *e.g.* in 257 pts. at 16° . Pure chloroform dissolves it very easily at the boiling heat, and deposits it almost completely on cooling. Alcoholic chloroform (2 vol. chloroform to 1 vol. of 90 per cent. alcohol) dissolves it easily even in the cold.

From whichever of these solutions the crystals may be obtained, they always contain $9H^2O$, as previously found by Howard (2nd Suppl. 345). The crystallisation of the salt from chloroform with so large a quantity of water arises from the circumstance that in the anhydrous state it absorbs water very rapidly. It cakes together, and gives off its water of crystallisation at 95° , and melts at about 149° to a yellow-brown liquid which soon becomes dark brown.

The *hydriodide*, obtained by decomposing the aqueous solution of the oxalate with potassium iodide, separates in crystals which may be purified by crystallisation from water. It then forms delicate yellowish needles having the composition $C^{20}H^{24}N^2O^7 \cdot HI + H^2O$, easily soluble in water, alcohol, and chloroform, and melting below 100° to a yellow-brown mass.

The *platinochloride*, $C^{20}H^{24}N^2O^7 \cdot 2HCl \cdot PtCl^4 + 2H^2O$, separates on mixing a slightly warmed and strongly acid solution of the hydrochloride with platinum chloride, in nodular groups of small, dark, orange-yellow needles. Howard describes this salt as anhydrous (2nd Suppl. 345); according to Hesse, the water of crystallisation escapes very easily.

The *aurochloride* is a yellow flocculent precipitate, which when heated partly melts and partly dissolves. The *mercurochloride* is obtained by double decomposition as a yellowish-white flocculent precipitate, which dissolves easily in hydrochloric acid, is

slightly soluble in cold, readily in hot water, and crystallises from the latter solution on cooling in small pale yellow needles often united in warty groups.

The *thiocyanate*, $C^{10}H^{12}N^2O^2 \cdot MCNS$, is obtained by mixing a warm aqueous solution of quinine oxalate with potassium thiocyanate, and crystallises in long, nearly white prisms, containing $\frac{1}{2}$ mol. H^2O . It dissolves easily in chloroform and alcohol, with moderate facility in water, but is insoluble in potassium thiocyanate, so that quinine is completely precipitated from its aqueous solution by excess of the thiocyanate: in that case, however, the salt first separates as an oil, which afterwards solidifies (Hesse).

Acetyl-quinine, $C^{10}H^{12}(O^2H^2O)N^2O^2$, is prepared by heating 1 part of quinine or quinidine with two parts of acetic anhydride to gentle boiling for three hours, evaporating over the water-bath, dissolving the residue in warm water, and fractionally precipitating with potash. The second fraction thus obtained dissolves readily in ether, and on evaporating the ether, the acetylated base remains as a clear uncrystallisable varnish which yields uncrystallisable salts. It appears to be somewhat deficient in power of combining with acids, not taking up a sufficient quantity of an acid to form a normal salt: thus a platinochloride obtained by adding platonic chloride to a solution of the base in a slight excess of hydrochloric acid, gave in two samples, 21.18 and 18.28 per cent. platinum, whereas the normal salt, $C^{10}H^{12}(C^2H^3O)N^2O^2 \cdot 2HCl \cdot PtCl^4$, requires 25.38, and the acid salt, $2(C^{10}H^{12}(C^2H^3O)N^2O^2 \cdot HCl) \cdot PtCl^4$, 17.44 per cent.

By saponifying this acetylated base with alcoholic soda, a base is obtained agreeing in composition and optical rotatory power with ordinary quinine, though somewhat altered by the high temperature employed in the acetylation process.

Apodiquinine, $C^{10}H^{12}N^2O^2 = 2C^{10}H^{12}N^2O^2 - H^2O$ (Hesse's *diconchinine**). This base constitutes the greater part of the amorphous base forming the quinidine of commerce (v. 26); it is wholly amorphous, and forms only amorphous salts. It is fluorescent in sulphuric acid solution, and, like quinine and quinidine, it gives a green coloration with chlorine and excess of ammonia. Dextrorotatory.

QUINAMINE GROUP.

Quinamine, $C^{10}H^{12}N^2O^2$ (formerly regarded by Hesse as $C^{10}H^{12}N^2O^2$), occurs in the bark of *C. succirubra*, from Darjeeling, and other localities in British India and Java; in the '*Cinchona rouge de Mutis*,' of Delondre; in *C. nitida*, *C. erythrantha*, *C. erythroderma*, *C. rosulenta*, *C. calisaya*, var. *Schuhkraffi*, and *C. calisaya*. De Vrij found it only in the cinchona bark from British Sikhim, not in other red Indian barks (*Pharm. J. Trans.* [3], iv. 609). It is difficult to separate from the amorphous alkaloïds, but the separation may be effected by means of potassium thiocyanate added to the solution of the mixed bases in acetic acid until the liquid is almost decolorised, when most of the amorphous bases are precipitated, with but little quinamine; on treating the residue left by the evaporation of the ethereal extract with ammonia and ether, and dissolving in alcohol, a liquid is obtained, from which quinamine crystallises on standing. It melts at 172° (Hesse).

Quinidine (Hesse's *conquinamine*) accompanies quinamine in *C. succirubra* and *rosulenta* barks; crystallises in long shining prisms, melting at 123° . Dextrorotatory. A solution of 1.8 grams in 100 c.c. of 97 per cent. alcohol gives at 16° the value $[\alpha]_D = +200$. Precipitated by platonic chloride only in concentrated solutions; the gold salt soon decomposes; the hyriodide crystallises in fine prisms.

Quinidine and **Quinamine** are two amorphous bases isomeric with quinamine, formed by heating quinamine with dilute sulphuric acid. The hydrochlorides are crystalline.

By continuing the action of sulphuric acid at 120° – 130° , a brownish, non-crystalline base is formed, precipitable by sodium carbonate and insoluble in ether. To this base, called *Proto-quinamine*, Hesse assigns the formula $C^{10}H^{12}N^2O^2$.

Apoquinamine, $C^{10}H^{12}N^2O$, isomeric with homo-cinchonine, is prepared by boiling quinamine or quinidine for a short time with hydrochloric acid. It is white, amorphous, easily soluble in ether, alcohol, and dilute hydrochloric acid, precipitated from the last solution by strong hydrochloric or by nitric acid. The hydrochloride, aurochloride and platinichloride are amorphous.

ALKALOÏDS NOT INCLUDED IN THE PRECEDING GROUPS.

and **Arctine**, $C^{20}H^{24}N^2O^4$ (Hesse, *Liebig's Annalen*, clxxv. 296). These bases are obtained from a Cusco cinchona-bark, apparently identical with that examined by Liverköhn (*Rep. Pharm.* xxxiii. 367), who found it to contain arctine.

* The name '*apodiquinine*' is suggested by Wright (*Chem. Soc. J.* xxxiv. 435), on the ground that the base in question resembles quinine more nearly than quinidine. The prefix '*apo*' is used generally to denote the formation of compounds by elimination of water (*1st Suppl.* 889; *2nd Suppl.* 822).

This bark gives off brown vapours when heated, and yields at last a brown tar, thereby differing from barks containing quinine or isomeric alkaloids, all of which give off red vapours when heated. Besides aricine and cusconine it contains a small quantity of an amorphous alkaloid, which Hesse believes to be derived from the other two. These bases do not exist in the bark in the free state, since they cannot be extracted by chloroform. They were isolated in the following manner:—An alcoholic extract of the comminuted bark was supersaturated with soda and shaken with ether; and the ethereal liquid was agitated with acetic acid, which took up the greater part of the alkaloids. The acetic solution was partially neutralised with ammonia, which threw down aricine acetate, and the filtrate from this substance was then mixed with a strong solution of ammonium sulphate, whereupon the cusconine was precipitated as sulphate. The mother-liquor contained the amorphous alkaloid, which has not been further examined. The percentage of alkaloids contained in the bark was about 0·62 of aricine, 0·93 of cusconine, and 0·16 of amorphous substance.

CUSCONINE is thrown down from the sulphate by ammonia as an amorphous precipitate, crystallising from ether in white laminae, and from alcohol or acetone in larger crystals. It dissolves in 35 times its weight of ether, more easily in alcohol and acetone, and very freely in chloroform, but is nearly insoluble in water. Strong nitric and sulphuric acids dissolve it with greenish coloration. A little cusconine added to a warm solution of *ammonium molybdate* in strong sulphuric acid colours it a dark blue, changing to olive-green when heated, and again turning blue as the liquid cools. This reaction is characteristic of cusconine and aricine. Cusconine rotates a ray of polarised light to the left; in the ethereal solution ($\alpha_D = -27^\circ$). The formula of the crystallised substance is $C^{22}H^{26}N^2O^4 + 2H^2O$, the water being given off at 80° . The anhydrous alkaloid melts at 110° . It is a weak base, forming salts which have a more or less acid reaction. The following have been prepared:—

Neutral sulphate, $2C^{22}H^{26}N^2O^4 \cdot SO^4H^2$. Crystallises from alcohol in laminae. The acid sulphate is gelatinous and uncrystallisable.

Hydrochloride.—Not crystallisable. Forms with mercuric chloride a white pulverulent precipitate.

Platinochloride, $2(C^{22}H^{26}N^2O^4 \cdot HCl) + PtCl^4 + 6H^2O$.—Amorphous, flocculent, dark-yellow precipitate.

Aurochloride.—Dirty-yellow amorphous flocculent precipitate, decomposing when warmed.

Hydrobromide.—Colourless; amorphous; soluble in water, from which it is precipitated by potassium bromide.

Hydriodide.—Pale-yellow amorphous precipitate, freely soluble in water, but sparingly soluble in solution of potassium iodide.

Thiocyanate, $C^{22}H^{26}N^2O^4 \cdot CNSH + 2H^2O$.—Pale yellow amorphous powder.

The *nitrate*, *acetate*, *citrate*, *tartrate*, *oxalate*, *thiosulphate*, and *salicylate* are all gelatinous and non-crystallisable.

ARICINE is obtained in the free state by decomposing the acetate with soda. It crystallises in white prisms, which dissolve very easily in chloroform, and less freely in ether and alcohol, but not in water. It melts at 188° , and decomposes at higher temperatures. With strong nitric and sulphuric acids it behaves in the same manner as cusconine. Its taste is slightly astringent, not bitter. In alcoholic or ethereal solution it rotates a ray of polarised light to the left. Analyses of aricine lead to the formula $C^{22}H^{26}N^2O^4$, which is the same as that of anhydrous cusconine. The neutral salts have a more or less acid reaction, and are partially decomposed by water. Their solutions turn yellow after a time, the alkaloid becoming converted into a coloured amorphous substance.

The *hydrochloride*, $C^{22}H^{26}N^2O^4 \cdot HCl + H^2O$, separates from its aqueous solution, on evaporation, in the form of a jelly, which afterwards crystallises.

The *platinochloride*, $2(C^{22}H^{26}N^2O^4 \cdot HCl)PtCl^4 + 6H^2O$, is an amorphous, orange-coloured precipitate, sparingly soluble in water.

The *aurochloride* is a dirty-yellow amorphous precipitate, easily decomposed.

The *neutral sulphate*, $2C^{22}H^{26}N^2O^4 \cdot SO^4H^2$, is precipitated as a white gelatinous mass, made up of delicate needles.

The *acid sulphate* is thrown down in small white prisms on adding sulphuric acid to a solution of the hydrochloride.

The *neutral oxalate* is a granular white crystalline powder.

The *acid oxalate*, $C^{22}H^{26}N^2O^4 \cdot O^2H^2O^4 + H^2O$, is precipitated by oxalic acid from a solution of the hydrochloride. It crystallises in prisms, which soon change to rhombohedrons. The salt requires for solution 2025 parts of water at 18° , and hence affords a means of separating aricine from cusconine.

The *nitrate*, $C^9H^8N^2O^4 \cdot NO^3H$, is precipitated by nitric acid from a warm solution of the hydrochloride. It forms delicate white prisms, easily soluble in alcohol. *

The *hydrobromide* is a white amorphous powder. The *hydriodide* forms small white prisms.

The *thiocyanate*, $C^9H^8N^2O^4 \cdot CNSH$, crystallises in small white prisms.

The *salicylate*, $C^9H^8N^2O^4 \cdot C^7H^4O^4 + 2H^2O$, is a pale yellow pulverulent precipitate, sparingly soluble in water, easily in alcohol.

The *acetate*, $C^9H^8N^2O^4 \cdot C^2H^4O^2 + 3H^2O$, is obtained by precipitating the hydrochloride either with sodium acetate or with acetic acid, a reaction which distinguishes aricine from all other alkaloids. It forms white granular crystals, very sparingly soluble in cold water. At 100° the acid is expelled, leaving the free alkaloid.

The *acid citrate* and the *neutral tartrate* are both crystalline salts.

Aricine, formerly regarded by Hesse as identical with cinchonidine (*Liebig's Annalen*, clxxx. 53), was first obtained in 1829 by Pelletier & Corriol (i. 357) from certain barks which are now very scarce. From one of these, *Cinchona pelletterana*, it has also been prepared by D. Howard (*Chem. Soc. J.* 1875, 309), whose description of its properties agrees in the main with that of Hesse above given. The specific rotatory power of the base in alcoholic solution he finds to be equal to -63° for the yellow ray.

Cusconidine is an amorphous alkaloid accompanying cusconine.

Paricine, $C^9H^8N^2O$, is an amorphous base, forming amorphous salts, which occurs, together with quinamine, in *C. succirubra* bark from Darjeeling. On keeping, it becomes less readily soluble in ether (2nd Suppl. 347).

Paytine, $C^9H^8N^2O \cdot H^2O$, occurring in white cinchona-bark from Payta in Peru, crystallises in fine prisms; levorotatory (*loc. cit.*)

Paytamine is an amorphous alkaloid accompanying paytine.

Javanine, from *C. Calisaya*, var. *Javanica*, crystallises from water in rhombic plates, dissolves very readily in ether, but does not separate from the solution in the crystalline form on evaporation. It forms an oxalate crystallising in lumines, and dissolves gradually in sulphuric acid with deep yellow colour.

Young *Calisaya* bark from Bolivia contains a fluid alkaloid, which makes spots on paper, has a pungent odour like that of chinoline, and is probably volatile (Hesse).

CINNAMENE, $C^9H^8 = C^9H^7 - CH=CH^2$. *Ethenyl-benzene*, *Vinyl-benzene*, *Phenyl-ethylene*, *Styrolene*, *Styrol*. This hydrocarbon is formed, together with other products, by heating phenyl-bromethyl, $C^6H^5 - CHBr - CH^2$, with an alcoholic solution of potassium cyanide, part of it being obtained in the liquid, partly in the solid modification (meta-cinnamene);—also together with acetic acid, by fractional distillation of secondary phenyl-ethyl acetate:



(Radziszewski, *Deut. Chem. Ges. Ber.* vii. 140).

Cinnamene (styrolene) from storax has hitherto been supposed to be optically active, exerting a laevogyrate power of 3° in a column 100 mm. long, whereas cinnamene from cinnamic acid is inactive (1st Suppl. 465). According to van't Hoff, however (*Bull. Soc. Chim.* [2], xxv. 175), cinnamene from storax is likewise inactive, the rotatory power observed in it by Berthelot having been due to the presence of a small quantity of a strongly laevogyrate substance, styrocamphene, $C^9H^{10}O$ or $C^9H^{10}O$, which van't Hoff has lately separated from volatile oil of storax, by converting the cinnamene contained therein into solid meta-cinnamene. Berthelot, on the other hand (*ibid.* 197), infers from new experiments that styrolene possesses a laevogyrate power of 3.1 to 3.4 .

In the mixture of hydrocarbons which Berthelot obtained by passing a mixture of cinnamene and benzene through a red-hot tube (1st Suppl. 466), Barbier has found phenanthrene as well as anthracene (*Jahresh.* 1874, 360).

Cinnamene bromide, $C^9H^7Br^2 = C^6H^5 - CHBr - CH^2Br$, is easily formed by heating 2 mols. bromine with 1 mol. ethyl-benzene to 145° – 150° . It crystallises from ether in indistinct prisms or needles, melts at 68° – 69° , and decomposes spontaneously in the dry state; in contact with water it does not decompose even on exposure to sunshine. When heated with water, to 190° , however, it is resolved into HBr and bromocinnamene, $C^6H^5 - CBr=CH^2$. When the vapour of cinnamene bromide is passed through a tube filled with quicklime and heated to low redness, acetonyl-benzene, $C^6H^5 - C \equiv CH$ (p. 8), is formed, together with a compound (m. p. 119°) whose solution in benzene is coloured red by picric acid. The alcoholic solution of this compound, on the other hand, is neither coloured nor precipitated by picric acid (Radziszewski, *Ber.* vi. 492).

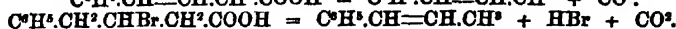
3rd Sup.

K, K

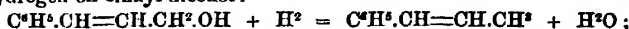
CINNAMENE, HOMOLOGUES OF. (Perkin, *Chem. Soc. J.* 1876, ii. 660.)

These hydrocarbons are formed by the dry distillation of acids homologous with cinnamic acid, or more readily in most cases by subjecting the hydrobromides or hydriodides of the same acids to the action of alkalis or alkaline carbonates, whereby HBr or HI is removed as well as CO₂. The hydrobromide of the acid is stirred up for some time with excess of a cold solution of sodium carbonate; the creamy mixture thereby produced is warmed to facilitate the formation of a layer of hydrocarbon on the surface; and this layer is collected, distilled with vapour of water, and dried.

Allyl-benzene, $C^6H^{10} = C^6H^5.CH=CH.CH^3$, is prepared by the processes just mentioned from phenylcrotonic acid or its hydrobromide:



The same hydrocarbon was obtained in 1873 by Fittig, Krügener & Rügheimer (*Ber.* vi. 214) in small quantity, together with phenyl-propyl alcohol, by the action of nascent hydrogen on cinnyl alcohol:



and in 1874 by Radziszewski (*ibid.* vii. 143) by passing bromine-vapour into normal propyl-benzene heated to 150°–160°, and boiling the resulting phenyl-propyl bromide, $C^6H^5(C^6H^5)Br$ or $C^6H^5.CHBr.CH^2.CH^3$, whereby it was resolved into HBr and allyl-benzene.

Allyl-benzene is a colourless, mobile, strongly refractive liquid, having a fragrant odour like that of cinnamene, and boiling at 165° (Fittig); 164°–166° (Radziszewski); 174°–175° (Perkin). It has a density of 0.9180 at 15°, does not solidify at 15°, and may be heated to 160°–200° for several hours without visible change. It colours strong sulphuric acid yellow, but is not appreciably dissolved by that acid. When boiled with strong nitric acid, it becomes yellow and heavier than water, and gives off red fumes (Perkin).

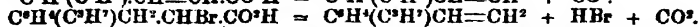
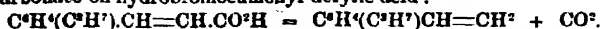
Allyl-benzene dibromide, $C^6H^{10}Br^2 = C^6H^5.CHBr.CHBr.CH^3$, is formed by direct combination. Radziszewski drops the calculated quantity of bromine into a solution of allyl-benzene in chloroform. Rügheimer adds bromine to well-cooled allyl-benzene till the colour no longer disappears: the product then solidifies after a while in the crystalline form. Perkin treats allyl-benzene with bromine-water in excess, washes the product with a little alkali and cools it with a freezing mixture, whereupon it solidifies to a crystalline mass, which does not liquefy on returning to the ordinary atmospheric temperature. It may be purified by pressure between paper and crystallisation from alcohol. This dibromide is also produced by heating 1 mol. propyl-benzene with 2 mols. bromine to 160°. Products of higher boiling point are however formed at the same time, one of which, boiling at 220°, has the composition $C^6H^5(C^6H^5)Br$.

Allyl-benzene dibromide crystallises from alcohol in colourless shining needles or laminae, melting at 66.5° (Rügheimer); in long white silky needles melting at 65°–66° (Radziszewski); at 67° (Perkin); sublimes without decomposition when cautiously heated; dissolves very slightly in cold water, very freely in hot alcohol (Rügheimer). Treated with hot alcoholic potash, it yields potassium bromide and a brominated oil (Perkin).

Butenyl-benzene, $C^{10}H^{12} = C^6H^5.CH=CH.CH^2.CH^3$, is formed from phenylangelic acid in the same way as allyl-benzene from phenylcrotonic acid. It is a colourless oil boiling at 186°–187°, and having an odour somewhat like that of cinnamene. The dibromide, $C^{10}H^{12}Br^2$, is formed by the action of bromine-water on the hydrocarbon. The crude oily product solidifies when cooled, and may be purified by pressure and recrystallisation from alcohol. It crystallises in needles melting at 67°, and is decomposed by alcoholic potash, with formation of a brominated oil (Perkin).

Another modification of butenyl-benzene, $C^6H^5.CH^2.CH^2.CH=CH^2$, produced, together with diallyl and diphenyl, by the action of sodium on a mixture of benzyl chloride and allyl iodide, has already been described as phenyl-butylene (*2nd Suppl.* 945). It is a colourless aromatic oil, distilling between 176° and 178°, and having a specific gravity of 0.915 at 15.5° (Aronheim).

Isopropyl-vinyl-benzene or Isopropyl-cinnamene, $C^6H^5(C^6H^7)CH=CH^2$, is prepared either by distilling cumenyl-acrylic acid at 200°–210°, or by the action of sodium carbonate on hydrobromocumenyl-acrylic acid:

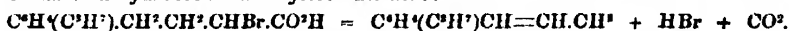


It is a colourless oil, which smells like cumic aldehyde, has a density of 0.8902 at 15°, and boils at 203°–204°, a considerable quantity however being polymerised during the

distillation and left behind. This change takes place in daylight at ordinary temperatures in the course of a month or two, more quickly indeed than that of cinnamene into metacinnamene, to which it is doubtless analogous. Isopropyl-cinnamene is scarcely acted upon by a solution of chromic acid, unless aided by heat. Iodine dissolves in it freely, and the solution when heated quickly solidifies to a tenacious mass.

The *dibromide*, $C^{10}H^{14}Br^2$, is easily formed by agitating the hydrocarbon with bromine-water, and is obtained by washing the product with dilute aqueous potash, and crystallisation from alcohol, in shining colourless needles melting at 71° . It dissolves freely in hot alcohol, and with moderate facility in cold alcohol. Heated with alcoholic potash it quickly decomposes, with separation of potassium bromide; and water added to the product throws down a heavy oil, probably $C^{10}H^{14}Br$, which when heated to about 150° for several hours, becomes brown and viscid, and gives off hydrobromic acid.

Isopropyl-allyl-benzene, $C^{12}H^{16}$, is best prepared by the action of sodium carbonate on hydrobromocumenylcrotonic acid:—



It has a density of 0.8900 at 15° , boils at 229° – 230° , does not solidify at -15° ; is not apparently altered by heating to 160° – 200° for sixty hours. It dissolves but sparingly in strong sulphuric acid even when heated, but is apparently polymerised; for, on adding water to dilute the acid, the oil which separates on the surface becomes quite thick on cooling.

The *dibromide*, $C^{12}H^{16}Br^2$, prepared like that of isopropyl-cinnamene, gradually solidifies to a crystalline mass, which must be strongly pressed to free it from a brominated oil, then left to dry to a white wax-like cake, and finally crystallised from alcohol. It melts at 59° to a colourless oil, which crystallises beautifully on cooling, dissolves easily in boiling alcohol, and crystallises therefrom in thin plates, very soluble in ether and in petroleum-spirit. Heated with alcoholic potash, it quickly decomposes, forming potassium bromide and a heavy brominated oil.

Isopropyl-butenyl-benzene, $C^{12}H^{18} = C^6H^5(C^2H^5).CH=CH.CH^2.CH^2$, prepared like the preceding, from hydrobromocumenylangelic acid, is a colourless oil having an odour like that of cumic aldehyde, but more fruity and less powerful. It has a density of 0.8875 at 15° , and boils at 242° – 243° ; does not thicken or undergo any apparent change when heated to 160° – 200° for several hours. When kept in contact with the air, however, it resinises. On shaking it with strong sulphuric acid, it becomes hot, and acquires a brown colour, which disappears on addition of water, and an oil then rises to the surface, which thickens on cooling. This thick oily product, most probably a polymeride, is nearly insoluble in alcohol. Isopropyl-butenylbenzene dissolves in fuming nitric acid with violent action, and, on adding water, a yellow oil separates which thickens on cooling.

The *dibromide*, $C^{12}H^{18}Br^2$, melts at 77° , dissolves very easily in benzene, ether, petroleum-spirit, and boiling alcohol, and separates from the latter in transparent plates on cooling. Heated with alcoholic potash, it yields KBr and a brominated oil.

CINNAMYDROXAMIC ACID. See HYDROXYLAMINE.

CINNAMIC ACID, $C^9H^8O = C^6H^5.CH=CH.CO^2H$. *Phenyl-acrylic acid* (Perkin, *Chem. Soc. Jour.* 1877, i. 389).—This acid is produced by heating benzaldehyde with acetic anhydride and sodium acetate:—



The mode of action is not very well understood, but the presence of sodium acetate or some analogous salt, as sodium valerate or lead acetate, appears to be essential. The transformation is best effected by heating 1 pt. of sodium acetate, 2 pts. benzoic aldehyde, and 3 pts. acetic anhydride in a sealed tube to about 180° for five or six hours. On opening the tubes, carbonic anhydride escapes (proceeding from the decomposition of part of the cinnamic acid produced), and a crystalline mass is found, containing a large proportion of cinnamic acid, sometimes as much as 84 per cent. of the benzaldehyde employed. To purify the product, it is boiled with water in a retort, any unconverted benzaldehyde being then carried over with the steam, and the residue is left to cool, during which time the crude oily cinnamic acid solidifies, and any that may be dissolved in the aqueous solution separates out. It is then collected on a filter, washed with water to remove sodium acetate, boiled with sodium carbonate, and after cooling, filtered from the oily impurities which are always present. On acidifying the solution, the cinnamic acid separates as a white crystalline precipitate, which may be further purified by two or three crystallisations from boiling alcohol.

The crystalline mass to which the contents of the tubes solidify on cooling is inter-

spersed with small pale-coloured opaque nodules consisting of *acid sodium cinnamate*, $C^6H^7NaO^2.C^6H^5O^2$, analogous to acid potassium benzoate. This salt dissolves in acetic anhydride, is decomposed by water, yielding cinnamic acid and sodium cinnamate, and dissolves in strong aqueous ammonia without forming cinnamide (Perkin).

Cinnamic acid unites at low temperatures with fuming *hydrobromic* and *hydriodic acids*; the addition-product separating out before complete solution has taken place. After several days standing and frequent agitation the conversion is complete. The resulting acids when moist are easily altered by heat, and they are very quickly decomposed by boiling with water. They may be purified by drying over sulphuric acid and solid potash, and crystallisation from carbon sulphide.

Hydrobromocinnamic acid, $C^6H^5BrO^2 = C^6H^5.CH^2.CHBr.CO^2H$, is formed also by the action of hydrobromic acid on phenyl-lactic acid, $C^6H^5O^2 + HBr = C^6H^5BrO^2 + H^2O$ (Glaser, *Liebig's Annalen*, cxlvii. 96; *comp. 1st Suppl.* 468). It forms colourless nacreous plates, very slightly soluble in carbon sulphide; melts at 138° ; begins to decompose at 143° ; and if heated for a long time on a paraffin bath, at a temperature not exceeding 150° , in a slow stream of air, it splits up almost quantitatively into hydrobromic and cinnamic acids. On boiling it with water, two simultaneous reactions take place, one part of the compound simply giving off hydrobromic acid, and yielding cinnamic acid, while in another part bromine is exchanged for hydroxyl, and phenyl-lactic acid is formed. This is an excellent method for the preparation of the last-named acid.

When hydrobromocinnamic acid is treated with ten times its weight of water (to keep down the heat of the reaction), and sodium carbonate is added to alkaline reaction, sodium carbonate and bromide are formed, and cinnamene collects on the surface as a colourless oil:



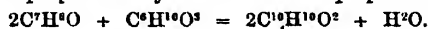
(F. Binder, *Deut. Chem. Ges. Ber.* ix. 1195).

Hydriodocinnamic acid, $C^6H^5IO^2$, resembles the brominated acid, but dissolves more readily in carbon sulphide, and melts, with blackening, at 119° – 120° (Binder).

CINNAMIC ACID, HOMOLOGUES OF, AND ALLIED ACIDS (Perkin, *Chem. Soc. Jour.* 1877; i. 391; ii. 661). These acids are obtained by heating benzoic aldehyde, and other aldehydes of the aromatic group, with the homologues of acetic anhydride and the sodium salts of the corresponding acids. The presence of these salts appears to be indispensable to the process, but, as in the case of cinnamic acid (p. 499), their mode of action is not yet understood. The best proportions of the materials are 2 pts. of the aldehyde, 2 pts. of anhydride, and 1 pt. of sodium salt, the mixture being heated in a sealed tube to 140° – 150° for twelve hours.*

* I. ACIDS $C^6H^{2n-10}O^2$, HOMOLOGOUS WITH CINNAMIC ACID.

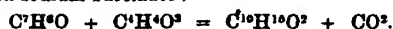
Phenyl-crotonic acid, $C^{10}H^{10}O^2 = C^6H^5.C^4H^5.CO^2H$, is prepared by heating benzoic aldehyde with propionic anhydride and sodium propionate:



The tubes when cold contained a nearly solid crystalline mass moistened with an oily product, and carbonic anhydride escaped on opening them. The product was mixed with water, freed from oily matter in the manner above described for cinnamic acid, then decomposed with hydrochloric acid, and the white precipitate washed on a filter with cold water, and twice crystallised from alcohol.

Phenyl-crotonic acid melts at 82° to a clear oil, and solidifies on cooling to a beautifully crystalline mass. It dissolves easily in alcohol, especially when hot, and separates on cooling in transparent oblique crystals. It is slightly soluble in boiling water, and crystallises on cooling in slender needles. Its *barium salt*, $(C^{10}H^9O^2)^2Ba + H^2O$, obtained by boiling the acid with baryta-water, separates on cooling in fern-like crystals, appearing when magnified to consist of plates. When dried in the water-oven, they lose their water and become opaque. They are but slightly soluble in boiling water.

Isophenyl-crotonic acid, $C^{10}H^{10}O^2$, is formed by heating benzaldehyde with succinic anhydride and sodium succinate:

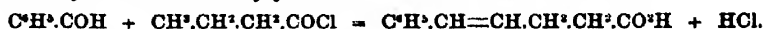


* In the earlier experiments, a larger proportion of anhydride was used, viz. 3 pts. to 2 pts. of the aldehyde, and the mixture was heated for about six hours to 160° – 180° ; but later experience has shown that better results are obtained with the smaller quantity of anhydride and the lower temperature above mentioned, the amount of carbon dioxide formed being thereby diminished and the yield of the acids increased.

The product is a brownish-red sticky substance melting, when boiled with water, to a thick red-brown oil, and yielding a pale yellow solution, which on cooling gradually deposits isophenyl-crotonic acid in leafy plates or long needles. These, when washed and afterwards boiled with water, melt at first to an oil, but afterwards dissolve for the most part, and the solution on cooling deposits the acid in beautiful white needles.

Isophenyl-crotonic acid melts at 83°-84°, and when strongly heated gives off suffocating vapours somewhat like succinic acid. The fused acid solidifies on cooling to a beautiful crystalline mass. It is excessively soluble in alcohol. The *silver salt*, $C^6H^5AgO^2$, is obtained as an extremely bulky and curdy precipitate on adding silver nitrate to a solution of 2 mols. of the acid and 1 mol. of sodium carbonate, filtering off the resulting precipitate, and treating the filtrate with excess of silver nitrate.

Phenyl-angelic acid, $C^{11}H^{12}O^2 = C^6H^5.C^4H^3.CO^2H$, was discovered by Fittig & Bieber (*Zeitschr. f. Chem.* 1869, 232), who obtained it by heating equal parts of benzaldehyde and normal butyryl chloride in sealed tubes to 120°-130°:



The crystalline mass thereby obtained was boiled with dilute sodium carbonate, and the phenyl-angelic acid separated from the solution by hydrochloric acid was converted into calcium or barium salt, and reprecipitated by hydrochloric acid. Perkin prepares the acid similarly to phenyl-crotonic acid, by prolonged heating of benzaldehyde with butyric anhydride and sodium butyrate; the purification is effected in the same manner as that of phenyl-crotonic acid.

Phenyl-angelic acid melts at 104° to a colourless liquid, and crystallises on cooling in small needles melting at 81°. It dissolves but very sparingly in cold water, more easily in hot water, and crystallises in long slender colourless needles. It is very soluble in alcohol, and separates therefrom in small white needles, but the mother-liquors, on standing, sometimes yield transparent crystals several millimeters in diameter. It dissolves easily in hot petroleum-spirit, but only slightly in the same liquid when cold. When boiled with water, it volatilises to a slight extent with the steam. Its *silver salt* is a white precipitate slightly soluble in cold water (Perkin). The *barium salt*, $(C^{11}H^{11}O^2)^2Ba$, crystallises in fern-like groups of needles, moderately soluble in cold, more soluble in hot water. The *calcium salt*, $(C^{11}H^{11}O^2)^2Ca$, exhibits similar characters. By oxidation with chromic acid mixture, the acid is converted into benzaldehyde and benzoic acid (Fittig & Bieber).

Phenyl-angelyl chloride, $C^{10}H^{11}O.COCl$, is prepared by gently warming a mixture of phenyl-angelic acid and phosphorus pentachloride, in the proportion of 1 mol. of each, heating the product to 140° after the first energetic action is over, and passing dry air over it to remove the phosphorus oxychloride. The product is a pale yellow oil, which is gradually decomposed by water, forming a crystalline mass of phenyl-angelic acid; with alcohol it yields an oily ether (Perkin).

Phenyl-angelamide, $C^{10}H^{11}.CONH^2$, is obtained by agitating the chloride with strong aqueous ammonia, as a yellowish white mass, to be purified by washing, drying, and solution in boiling alcohol, from which it separates on cooling in very beautiful prismatic crystals. It dissolves easily in alcohol, with some difficulty in petroleum-spirit, slightly in boiling water, from which it crystallises on cooling. It melts at 128° (Perkin).

Cumenylacrylic or Isopropyl-phenylacrylic acid, $C^{12}H^{14}O^2 = C^6H^5(C^3H^7).C^2H^3.CO^2H$, is obtained by heating cumic aldehyde with sodium acetate and acetic anhydride:



The product is a pale brown radio-crystalline mass, from which, by boiling with water, treatment of the resulting solution with hydrochloric acid, &c., as described for the preceding compounds, and repeated crystallisation from alcohol, cumenyl-acrylic acid is obtained in white needles apparently consisting of oblique prisms. It dissolves freely in alcohol and in hot glacial acetic acid, but is only slightly soluble in boiling water. It melts at 157°-158° to a clear liquid which solidifies to a crystalline mass on cooling. When heated till it boils, it is resolved into carbonic anhydride and isopropylcinnamene (p. 498). Cold fuming nitric acid dissolves it, forming a nitro-acid which crystallises from alcohol in yellow needles. Cumenyl-acrylic acid, heated with aqueous chromic acid, is gradually oxidised, and yields a distillate of cumic aldehyde. A solution of the acid in carbon sulphide, heated with bromine, yields a bromine derivative which is decomposed by heating with alkalis.

Ammonium Cumenylacrylate is obtained, by evaporating a solution of the acid in ammonia over sulphuric acid in a vacuum, as a mass of asbestos-like crystals, which give off ammonia with caustic alkalis; it is not easily soluble in water. The *sodium*

salt, obtained by boiling the acid with the calculated quantity of sodium carbonate, rises up to a white very indistinctly crystalline mass. It is moderately soluble in water, but is precipitated from its solution by sodium chloride; when strongly heated it gives off a considerable quantity of a hydrocarbon. Hydrochloric acid added to its solution throws down the cumenyl-acrylic acid as a snow-white flocculent powder. The *calcium salt*, $(C^{12}H^{10}O^2)_2Ca$, is obtained by adding calcium chloride to an aqueous solution of the sodium salt, as a white, bulky crystalline precipitate, and by recrystallisation from boiling water, in beautiful white needles. It is sparingly soluble in water. Heated to 90° – 100° in air free from carbonic acid, it quickly takes up oxygen in the proportion of nearly 1 at. O to 1 mol. of the salt, and on decomposing the oxidised salt with hydrochloric acid, a white, easily decomposable acid is obtained, probably consisting of oxycumenylacrylic acid, $C^{12}H^{10}O^3$. The *barium salt*, obtained by double decomposition, is a white powder, which appears to be slightly crystalline, and sometimes conglomerates to a plastic mass when boiled with water, in which it is slightly soluble. The *strontium salt*, $(C^{12}H^{10}O^2)_2Sr + 2H^2O$, resembles the barium salt, being a white powder slightly soluble in water. The *copper salt* is a green precipitate; the *ferric salt*, a light brown precipitate. The *silver salt*, $C^{12}H^{10}O^2Ag$, obtained by adding silver nitrate to a hot solution of the sodium salt, separates as a copious bulky precipitate, which soon contracts and appears crystalline under the microscope; strongly electric when dry.

Cumenylacryl chloride, $C^{12}H^{10}.COCl$, is prepared by treating the acid with PCl^3 in calculated proportion, heating the product to 130° in an oil-bath to distil off the phosphorus oxychloride, and then passing dry air through it at the same temperature. On cooling, it solidifies to a crystalline mass melting at about 25° . It is quickly reconverted into the acid on exposure to the air, and when mixed with alcohol, yields a heavy oil doubtless consisting of ethylic cumenylacrylate.

Cumenylacrylamide, $C^{12}H^{10}.CONH^2$, obtained by the action of aqueous ammonia on the chloride, is a white powder, insoluble, or nearly so, in water, moderately soluble in alcohol, and crystallising therefrom in satiny plates not unlike laves of sublimed naphthalene. It melts at 185° – 186° , and when further heated, distils with evolution of small quantities of ammonia. Boiling aqueous potash does not decompose it, except in saturated solution, in which case ammonia is freely given off.

Hydrocumenylacrylic or *Cumenylpropionic acid*, $C^{12}H^{10}O^3 = C^2H^4(C^2H^7).CH^4.CO^2H$, is formed by the action of nascent hydrogen on cumenylacrylic acid. The acid mixed with about 15 times its weight of water was treated with sodium-amalgam (containing 2 per cent. sodium) in quantity sufficient to form its sodium salt; the mixture being frequently shaken, whereupon the acid dissolved with but little evolution of hydrogen; excess of sodium-amalgam was then added, and the mixture left for several hours till hydrogen was somewhat freely evolved. After the separation of the amalgam, the solution was acidified with hydrochloric acid, which threw down a crystalline precipitate of cumenylpropionic acid; and by washing his precipitate with water, pressing it between bibulous paper, then dissolving it in warm glacial acetic acid, filtering from a small quantity of an amorphous insoluble product, and gradually adding water to the clear filtrate, the phenyl-propionic acid was separated in satiny scales.

This acid melts at 70° to a clear oil, which crystallises very beautifully on cooling. It is very soluble in hot alcohol, petroleum-spirit, and glacial acetic acid, insoluble, or nearly so, in water. Its *sodium salt*, obtained by boiling the acid with sodium carbonate, forms a clear solution. The *barium* and *calcium salts* are white precipitates which become tenacious when rubbed with a glass rod. The *silver salt*, $C^{12}H^{10}AgO^2$, prepared by double decomposition with the sodium salt and silver nitrate, rejecting the first portions thrown down, is a white precipitate nearly insoluble in water.

Hydrobromocumenylacrylic acid, $C^{12}H^{10}BrO^2 = C^2H^4(C^2H^7).CH^2.CHBr.CO^2H$, is produced by leaving finely divided cumenylacrylic acid in contact for several days with fuming hydrobromic acid, sp. gr. 1.74,—or better by treating it with a saturated solution of hydrogen bromide in glacial acetic acid. On exposing the mixture to the air after the action is completed, the hydrobromocumenylacrylic acid separates out in crystalline crusts. This acid is very soluble in alcohol and in ether, and separates from the latter on evaporation in shining crystals. It melts at 85° – 87° , and when further heated decomposes with separation of hydrobromic acid. When boiled with water, it melts to an oil, and then becomes pasty, splitting up chiefly into hydrobromic and cumenylacrylic acids. Treated with a cold solution of sodium carbonate or caustic potash, it is resolved into HBr , CO^2 , and isopropylcinnamene, $C^{12}H^{14}$ (Perkin, *Chem. Soc. Jour.* 1877, ii. 661).

Cumenyl-crotonic acid, $C^{10}H^{10}O^2 = C^6H^4(C^2H^5).C^3H^3.CO^2H$, is produced by heating cumic aldehyde with sodium acetate and 3 pts. propionic acid, and purified in the same manner as the corresponding acids already described. It crystallises from alcohol in nodular masses, from petroleum-spirit in beautiful oblique prisms; melts at 90° – 91° , crystallises on cooling, and then swells up in a most remarkable manner into leaf-like scales. It dissolves easily in alcohol and in boiling petroleum-spirit, only slightly in the latter when cold. Its *silver salt*, $C^{10}H^{10}AgO^2$, prepared like that of isophenylcrotonic acid (p. 504), forms at first a copious white curdy precipitate, rendering the liquid semi-solid, but becomes denser after being stirred and left at rest.

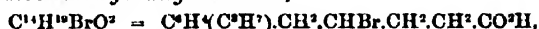
Hydromocumenylcrotonic acid,



prepared like hydromocumenylacrylic acid, crystallises in flat oblique prisms. It is extremely soluble in ether, moderately soluble in alcohol, benzene, and glacial acetic acid, sparingly in petroleum-spirit. It melts with partial decomposition at 140° – 150° , and, if more strongly heated, gives off large quantities of hydrobromic acid. It is decomposed by potash or by sodium carbonate, like hydromocumenylacrylic acid, yielding isopropylallylbenzene, $C^{10}H^{10}$ (p. 499).

Cumenyl-angelic acid, $C^{11}H^{12}O^2 = C^6H^4(C^2H^5).C^3H^3.CO^2H$, prepared from cumic aldehyde, butyric anhydride, and sodium butyrate or acetate, and purified like the preceding acids, is a crystalline substance melting at 123° , freely soluble in alcohol, especially when hot, and separating therefrom on cooling in colourless needles.

Hydromocumenyl-angelic acid,



prepared like its lower homologues, crystallises in flat prisms; is freely soluble in ether, moderately soluble in alcohol; decomposes when heated, giving off HBr; and is converted by alkalis, with loss of HBr and CO^2 , into isopropylbutenylbenzene, $C^{11}H^{12}$ (p. 499).

II. ACIDS, $C^9H^{10}-12O^2$, FROM CINNAMIC ALDEHYDE.

These acids are formed from cinnamic aldehyde, C^9H^8O , in the same manner as those of the preceding series from benzaldehyde and its homologues (Perkin, *Chem. Soc. Jour.* 1877, i. 403).

Cinnamonylacrylic acid, $C^{11}H^{10}O^2 = C^6H^5-C^2H^2=C^2H^2-CO^2H$, is prepared by heating cinnamic aldehyde (or cinnamon oil of the best quality) with acetic anhydride and sodium acetate. Carbon dioxide escapes on opening the tube, and, on mixing the product with water, the saline matter dissolves, leaving a resinous substance which dissolves but partially when boiled with aqueous sodium carbonate. The filtered alkaline solution, acidified with hydrochloric acid, gives a white precipitate of cinnamonylacrylic acid, which may be purified by crystallisation from alcohol, and then from petroleum spirit.

Cinnamonylacrylic acid dissolves easily in alcohol, and crystallises therefrom in thin plates: it is but slightly soluble in petroleum spirit, but separates from it in more distinct crystals. It melts at 165° – 166° . When heated and boiled it decomposes, yielding an oil which burns with a very smoky flame. When boiled with aqueous chromic acid it yields a distillate containing an oil which appears to be cinnamic aldehyde.

Sodium salt.—Cinnamonylacrylic acid dissolves slowly in a dilute boiling solution of sodium carbonate, and if theoretical quantities are employed, the solution, on evaporation, dries up to a white, almost amorphous mass, not very soluble in cold water.

The *calcium salt* is obtained by adding calcium chloride to a solution of the sodium salt, as a white precipitate, dissolving to a small extent in boiling water, from which it separates in small glistening crystals on cooling.

The *barium salt*, obtained in like manner, is a white precipitate, slightly soluble in water, and separating from the boiling solution on cooling in small needles.

The *magnesium salt* is a white milky precipitate, which redissolves almost immediately, but separates again in the crystalline state on standing.

The *silver salt* is a white, somewhat curdy precipitate, slightly soluble in water, blackening gradually in sunlight. The *lead salt* is a white curdy precipitate, the *copper salt* a pale green, the *ferric salt* a pale brown precipitate.

Cinnamonylacryl chloride, $C^{11}H^{10}OCl$, obtained by treating the acid with phosphorus pentachloride, separates from the fluid mixture on cooling, in small crystals, which render the whole nearly solid.

Cinnamenylacrylamide, $C^{11}H^{10}(NH_2)$, is obtained by agitating the chloride with strong aqueous ammonia, as a white substance insoluble in water, moderately soluble in alcohol, and crystallising therefrom in flat needles, like benzoic acid.

Hydrocinnamenylacrylic acid, $C^{11}H^{12}O_2$, was prepared by gradually adding

to an ethereal solution, the acid remained in the form of an oily liquid. The *silver salt*, $C^{11}H^{11}AgO_2$, is a white precipitate, giving by analysis 37.62 per cent. silver, the formula requiring 38.16 per cent. This analysis, and that of the acid (exp. 74.52 C, 6.68 H; calc. 75.0 C, 6.81 H) are not quite satisfactory; but if the formula $C^{11}H^{12}O_2$ be correct, the acid is isomeric with phenylangelic acid.

Cinnamenylcrotonic acid, $C^{12}H^{12}O_2 = C^6H^4.OH^2.C^2H^4.CO^2H$, was prepared by heating 15 pts. cinnamic aldehyde, 15 pts. propionic anhydride, and 6 pts. sodium propionate, and purified like cinnamenylacrylic acid. It is easily soluble in alcohol, insoluble in cold, sparingly soluble in hot petroleum spirit, and crystallises therefrom in flat oblique transparent prisms which become opaque on keeping. It melts at 157° – 158° .

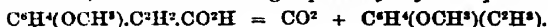
The *sodium salt* is obtained by prolonged boiling of the acid with a dilute solution of sodium carbonate, and remains, on evaporation in a vacuum, as a distinctly crystalline product, only moderately soluble in water. The *calcium* and *barium salts*, obtained by double decomposition, are white flocculent precipitates, sparingly soluble in boiling water, and deposited therefrom on cooling in groups of minute crystals. The *magnesium salt* is crystalline and more soluble than the last two. The *ferric salt* is a pale brown precipitate; the *copper salt* a very pale green precipitate. The *silver salt*, $C^{12}H^{11}AgO_2$, is pure white, slightly soluble in cold water, and is but slowly acted upon by light.

Cinnamenylangelic acid, $C^{13}H^{14}O_2 = C^6H^4.C^2H^4.CO^2H$, was prepared by heating cinnamic aldehyde with butyric anhydride and sodium butyrate to 160° – 165° , and purified in the manner described for the preceding acids. It did not, however, give satisfactory results on analysis, and was therefore further purified by conversion into the calcium salt, decomposition of this salt by hydrochloric acid, and crystallisation of the precipitate from petroleum spirit. It forms small shining crystals, melts at 125° – 127° , dissolves easily in alcohol, not very freely in petroleum-spirit. The *silver salt*, $C^{13}H^{13}AgO_2$, is a white precipitate slightly soluble in cold water.

III. ACIDS $C^8H^{2n-10}O_2$, FROM ANISIC ALDEHYDE.

Methyl-paraoxyphenylacrylic acid or **Methyl-paracoumaric acid**, $C^{10}H^{10}O_2 = C^6H^4(OCH^3).C^2H^2.CO^2H$, is prepared by heating 2 pts. anisic aldehyde (anisal) with 1 pt. sodium acetate and 2 pts. acetic anhydride; boiling the dark-coloured product till the distillate is nearly free from oil; leaving the residue to cool; washing the crystalline product on a filter to remove saline matter; then boiling it with sodium carbonate; passing the solution through a wet filter to remove neutral oily products; precipitating with hydrochloric acid; and twice recrystallising the washed and dried precipitate from alcohol.

Methyl-paraoxyphenylacrylic acid melts at about 171° . It is moderately soluble in alcohol, from which it crystallises in very pale yellow needles; sparingly soluble in boiling water, which deposits it, on cooling, in small white crystals. When heated till it boils, it decomposes, yielding an oil which has a strong but pleasant odour of fennel, and solidifies to a crystalline mass on cooling. This compound is probably a homologue of anethol, its formation being represented by the equation:



Methyl-oxyphenylacrylic acid, boiled in a retort with dilute chromic acid, is slowly oxidised, and yields an oily distillate, apparently consisting of anisal.

Metallic Methylphenyloxyacrylates.—The *sodium salt*, $C^{10}H^9NaO_2$, obtained by boiling the acid with the calculated quantity of sodium carbonate, is deposited on cooling as a white mass of microscopic satiny crystals, rather sparingly soluble in water. The *calcium salt* is obtained in transparent needles by adding calcium chloride to a weak boiling solution of the sodium salt, and leaving the liquid to cool. The *barium salt* is obtained in like manner as a crystalline precipitate. The *strontium salt* separates on cooling in small crystals, more soluble than the barium salt. The *copper salt* is a pale bluish-green precipitate; the *ferric salt*, a brown precipitate. The *silver salt*, $C^{10}H^9AgO_2$, is obtained as a pure white precipitate, slightly soluble in water, by adding silver nitrate to a dilute solution of the sodium salt, till a

slight precipitate is formed, and not redissolved on stirring, then filtering and treating the filtrate with excess of silver nitrate.

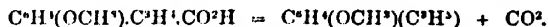
Methylparoxyphenylacryl chloride, prepared by the action of PCl_5 on the acid, and freed from POCl_3 by heating the product to 120° – 130° , and then passing dry air over it, is a dark yellowish oil which solidifies on cooling to a crystalline mass, melting at about 50° . With alcohol it yields the ethylic ether, as a pale yellow viscid oil heavier than water.

The amide, $\text{C}^{10}\text{H}^{10}\text{O}(\text{NH}_2)$, is formed by treating the chloride with alcoholic ammonia, whereupon it becomes hot and deposits crystals. On evaporating off the alcohol, and treating the residue with water, a white product is left, which may be purified by crystallisation from water. It melts at 180° , and crystallises on cooling. Alcohol dissolves it readily, and deposits it in scaly crystals. Water dissolves it but sparingly, and the crystals obtained from the solution are very small.

Hydromethyl-paroxyphenylacrylic or **Methylparoxyphenylpropionic acid**, $\text{C}^{10}\text{H}^{12}\text{O}_4 = \text{C}^6\text{H}_4(\text{OCH}_3) \cdot \text{C}^2\text{H}^4 \cdot \text{CO}_2\text{H}$, is formed by the action of sodium amalgam (containing 2 per cent. sodium) on a mixture of 1 pt. methylparoxyphenylacrylic acid and 50 pts. water, the mixture being constantly agitated till the whole of the acid has dissolved; excess of the amalgam is then added; the mixture left to itself for twenty-four hours; the clear solution then decanted, and acidified with hydrochloric acid; and the resulting white precipitate is washed on a filter with cold water, purified by solution in boiling water, and filtered from a small quantity of insoluble matter. The filtrate on cooling deposits the acid $\text{C}^{10}\text{H}^{12}\text{O}_4$ in feathery crystals melting at 101° .

Methylparoxyphenylcrotonic acid, $\text{C}^{11}\text{H}^{12}\text{O}_4 = \text{C}^6\text{H}_4(\text{OCH}_3)_p \cdot \text{C}^2\text{H}^4 \cdot \text{CO}_2\text{H}$, was prepared by heating anisic aldehyde with propionic anhydride and sodium propionate, and partly purified in the same manner as the preceding compounds; but the solution obtained by boiling the crude product with sodium carbonate being still milky, even after filtration, it was treated with ether, then boiled and acidified with hydrochloric acid. The acid $\text{C}^{11}\text{H}^{12}\text{O}_4$ then separated as a white precipitate, which was washed and crystallised from alcohol.

This acid is moderately soluble in alcohol, and crystallises therefrom in beautiful transparent rectangular plates. It melts at 154° , and decomposes when heated to boiling, yielding an oil which smells like oil of anise, and becomes crystalline on cooling. This oil is doubtless anethol, its formation being represented by the equation:



Calcium Methylparoxyphenylcrotonate, obtained by adding calcium chloride to a dilute solution of the sodium salt, is a crystalline precipitate which dissolves on boiling, and is deposited on cooling in small white needles. The **barium salt**, similarly prepared, crystallises from its boiling aqueous solution on cooling in thin shining needles. The **silver salt**, $\text{C}^{11}\text{H}^{11}\text{AgO}_4$, prepared like those of the acids previously described, is a satiny crystalline precipitate, slightly soluble in cold water, more soluble in hot water, from which it crystallises on cooling in slender needles. Light acts upon it but slowly.

Methylparoxyphenylangelic acid, $\text{C}^{12}\text{H}^{14}\text{O}_4 = \text{C}^6\text{H}_4(\text{OCH}_3)_p \cdot \text{C}^2\text{H}^4 \cdot \text{CO}_2\text{H}$, was prepared by heating a mixture of anisic aldehyde, butyric anhydride, and sodium butyrate, the product being purified similarly to the last, excepting that the treatment with ether was not required. It crystallises from alcohol in needles; melts at 123° – 124° to a colourless oil, and crystallises very beautifully on cooling. When heated to boiling it decomposes, with separation of CO_2 , yielding an oil smelling like oil of anise, and probably consisting of a homologue of anethol, $\text{C}^6\text{H}_4(\text{OCH}_3)_p(\text{C}^2\text{H}^3)$.

IV. ACIDS ISOMERIC WITH THE PRECEDING, OBTAINED FROM METHYLSALICYLIC ALDEHYDE AND FROM COUMARIN.

Methylorthoxyphenylacrylic acid, $\text{C}^{10}\text{H}^{10}\text{O}_3$. Of this acid there are two modifications, distinguished as α and β .

The α -acid is formed as α methyllic ether, $\text{C}^6\text{H}_4(\text{OCH}_3) \cdot \text{C}^2\text{H}^2 \cdot \text{CO}(\text{OCH}_3)$, by subjecting an alcoholic solution of sodium coumarate, $\text{C}_8\text{H}_7(\text{ONa}) \cdot \text{C}^2\text{H}_2 \cdot \text{CO}(\text{ONa})$ —obtained by boiling coumarin with caustic soda (see COUMARIN)—to the action of methyl iodide at 100° in a sealed tube for about three hours.* The product, freed from alcohol by distillation and mixed with water, yields the methyllic ether, $\text{C}^{10}\text{H}^{10}\text{O}_3$, as an oil boiling at 278° – 280° ; and from this the acid $\text{C}^{10}\text{H}^{10}\text{O}_3$ may be obtained by boiling with potash, then adding water, boiling off the alcohol, and adding hydrochloric acid. The acid then separates as an oil, which crystallises on cooling and may be purified by recrystallisation from ordinary acetic acid, separating therefrom on cooling in glistening

crystals, which generally lose their lustre in drying. It is easily soluble in alcohol and melts at 88° – 89° .

The *sodium salt* is extremely soluble in water, and dries up to a gummy mass; the *silver salt* a white crystalline precipitate; the *copper salt* a bright yellowish-green precipitate; the *ferric salt* a pale brown precipitate.

β . *Methylorthoxyphenylacrylic acid* was prepared by heating methyl-salicylic aldehyde with acetic anhydride and sodium acetate in sealed tubes to 100° for about six hours, purifying the crystalline product in the usual way with sodium carbonate, decomposing the sodium salt with hydrochloric acid, and recrystallising from alcohol.

This acid is moderately soluble in alcohol, and crystallises therefrom in small hard prisms. It melts at 182° – 183° . Heated to boiling it decomposes, yielding an oil which has an odour very different from that of the oil obtained from the para-acid, but somewhat like that of coal-tar naphtha. The acid fused with potash first turns yellow, apparently in consequence of the formation of coumaric acid, but when further heated yields a large quantity of salicylic acid. Heated with phosphorus pentachloride, it yields a chloride, which is converted by ammonia into methylorthoxyphenylacrylamide, $C^6H^4(OCH^3)_2.C^2H^3.CONH^2$, crystallising from alcohol in needles and melting at 191° – 192° .

The *calcium* and *barium salts* are white precipitates which become crystalline; the *copper salt* is a green, the *ferric salt* a pale brown, and the *silver salt*, $C^6H^4AgO^2$, a white precipitate.

The β -compounds are also formed from the corresponding α -compounds by the action of heat. The α -acid is converted into the β -acid by heating it to its boiling point. The α -methyl ether undergoes a corresponding change at 150° – 165° , and if heated with alcoholic ammonia for ten or fourteen hours at 200° , it yields the β -amide melting at 191° – 192° . The same amide is produced by treating the α -acid with phosphorus pentachloride, and the resulting chloride with ammonia.

The difference of structure between the α - and β -acids has not yet been clearly made out.

The following table exhibits some of the differences of their properties:—

	I. Methylparoxy- phenylacrylic acid	II. β -Methylorthoxy- phenylacrylic acid	III. α -Methylorthoxy- phenylacrylic acid
Melting points	171°	182° – 183°	88° – 89°
Colour of ferric salt	Brown precipitate.	Pale brown precipitate.	Pale brown precipitate.
„ copper „	Pale bluish green precipitate.	Green precipitate, yellower and darker than I.	A bright yellowish-green precipitate, darker than I. and II.
1 p.c. solution of sodium salt, with $CaCl^2$ and $BaCl^2$	A crystalline white precipitate.	—	—
2½ p.c. solution of sodium salt, with $CaCl^2$ and $BaCl^2$	Ditto.	A white precipitate.	—
	A 2½ p.c. solution of the sodium salt deposits a large quantity of the salt on cooling in white satiny crystalline masses.	A 2½ p.c. solution of the sodium salt remains clear on cooling; the salt is deposited only on concentration, when it separates in crystals.	The sodium salt is excessively soluble in water, and, when evaporated, dries up to a gummy mass.

Methylorthoxyphenylcrotonic acid, $C^{11}H^{12}O^3 = C^6H^4(OCH^3)_2.C^2H^4.CO^2H$, prepared by heating methylsalicylic aldehyde with propionic anhydride and sodium propionate, and precipitated by hydrochloric acid, melts at 104° – 105° ; dissolves very freely in alcohol and benzene, easily in petroleum spirit, but from a boiling solution in this solvent it is deposited on cooling in large leafy crystals arranged in fern-like groups. When heated in a watch-glass, it melts to a clear oil, and crystallises

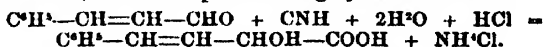
on cooling in small circular discs radiating from a centre, and as these increase, they crack with such force as to cause the watch-glass to emit a distinct sound each time. The crystalline mass often shows colours somewhat like those of mother-of-pearl.

The *calcium salt* separates as a white crystalline precipitate on adding calcium chloride to a solution of the sodium salt. If the solution be very dilute, it crystallises in beautiful groups of satiny needles; it is more soluble in hot than cold water. The *barium salt*, $(C^1H^{11}O^2)^2Ba$, separates in needles apparently containing water of crystallisation, on adding barium chloride to a somewhat dilute solution of the sodium salt, and leaving the solution to cool. It is rather soluble in cold water. The silver salt is a white precipitate slightly soluble in cold water.

Methylorthoxyphenylangelic acid, $C^{12}H^{14}O^3 = C^6H^4(OCH^3)_2.C^2H^2.CO^2H$, was prepared by heating a mixture of methylsalicylic aldehyde, butyric anhydride, and sodium butyrate, purified in the usual manner, and finally by conversion into calcium salt, precipitation with hydrochloric acid, and two crystallisations from alcohol. It then separated in hard needles about three-quarters of an inch long. It is very soluble in alcohol, much less freely in petroleum spirit. Melts at about 105° (Perkin).

CINNAMIC ALDEHYDE. CINNAMAL, $C^9H^8O = C^6H^5.CHO$. The pure aldehyde, prepared by treating oil of cassia or oil of cinnamon with an alkaline bisulphite, and decomposing the resulting crystalline compound by distillation with an alkali, boils at 247° – 248° (Perkin, *Chem. Soc. J.* 1877, i. 403).

CINNAMOMANDELIC or **PHENYLOXYCROTIC ACID**, $C^{10}H^{10}O^3 = C^6H^5-CH=CH-CHOH-COOH$ (Kaetsa Ukimori Matsumoto, *Deut. Chem. Ges. Ber.* viii. 1144). This acid is produced by prolonged boiling (forty to sixty hours) of 1 pt. of cinnamic aldehyde with 100 to 150 pts. water, 5 to 6 pts. of 12 per cent. hydrocyanic acid, and 7 to 8 pts. of strong hydrochloric acid:



The still lukewarm liquid is freed by filtration from unaltered cinnamic aldehyde, then evaporated to dryness, and the residue is treated with a small quantity of cold water to dissolve out the sal-ammoniac. On boiling the remaining portion with a small quantity of water, and filtering off the undissolved oil, the phenyloxycrotic acid separates in crystals contaminated with cinnamic acid, from which they may be freed by mixing the hot solution with ammonia and a slight excess of lead acetate, filtering it from the lead precipitate at boiling heat, and decomposing the hot filtrate with sulphuric acid. The yield does not exceed 4 or 5 per cent.

Phenyloxycrotic acid crystallises in colourless transparent needles, melting at 115° , slightly soluble in cold water, more readily in hot water, very easily in alcohol and in ether. Its *alkali-salts* are obtainable only as very deliquescent crystalline masses. Their solutions give with *silver nitrate* a white flocculent precipitate which soon turns black. The best crystallised phenyloxycrotonates are the barium and lead salts. The *barium salt* forms fine crystals, having, when dried at 100° – 110° , the composition $(C^{10}H^9O^3)^2Ba$. The *lead salt* crystallises from hot water in spherical groups of needles having the composition $(C^{10}H^9O^3)^2Pb + 2H^2O$; sparingly soluble in cold water, and melting at 190° to a transparent vitreous mass.

CITRACONIC ACID. See PYROCITRIC ACIDS.

CITRADIBROMOPYROTARTARIC ACID. See PYROTARTARIC ACID.

CITRAMALIC ACID. An isomeride of Oxypyrotartaric acid, $C^8H^8O^5$ (q.v.)

CITRATARTARIC ACID. See PYROCITRIC ACIDS.

CITRIC ACID, $C^6H^8O^7 = C^3H^4(OH).(CO^2H)^2$. This acid is now made almost entirely from lemon-juice prepared from windfalls and imperfect fruit. This juice, in its unconcentrated state, contains from 8 to 9 oz. of acid in the gallon; that expressed from the fruit imported into England contains from $10\frac{1}{2}$ to $12\frac{1}{2}$ oz. of acid. The concentrated juice usually contains about 64 per cent. of free citric acid per gallon, and 6 or 7 per cent. combined with bases; of the total acid about 8 per cent. consists chiefly of organic acids of the acetic series: the unconcentrated juice likewise contains malic and aconitic acids. Concentrated bergamot-juice is much less acid than lemon-juice, usually containing from 49.4 to 55.5 oz. per gallon. The acidity of raw lime-juice is about equal to that of English pressed lemon-juice (Warrington, *Chem. Soc. J.* 1875, 925–933).

Estimation of Citric acid in Lemon-juice.—No general method is known for separating citric acid from other organic acids; but as calcium citrate is insoluble in water, whereas the calcium salts of malic and aconitic acids, and of the volatile organic acids present, are soluble, a determination of the quantity of insoluble organic

salt obtainable from the juice will give the percentage of citric acid with sufficient accuracy for technical purposes. The following method is given by Warrington (*loc. cit.*):—15–20 c.c. of unconcentrated lemon-juice, or a quantity of concentrated juice equal to about 3 c.c., is exactly neutralised with pure caustic soda; the solution, which measures about 50 c.c., or is concentrated to that bulk, is brought to boiling in a salt-bath, and so much solution of calcium chloride is added as is known to be rather more than sufficient for the total organic acids present; the whole is then boiled for half an hour. The precipitate is collected and washed with hot water. As calcium citrate is rather soluble in water, the filtrate and washings are to be concentrated in the salt-bath to about 10–15 c.c., the solution being finally neutralised with a drop of ammonia if it has become acid. The second precipitate thus obtained is to be collected on a very small filter, the filtrate being used to transfer the precipitate to the paper, and the precipitate receiving only five or six washings with hot water. As a matter of precaution, the filtrate and washings may be evaporated a third time in the salt-bath. The precipitates, with their papers, are then burnt at a low red heat in a platinum basin, and the neutralising power of the ash determined by appropriate treatment with standard hydrochloric acid and alkali.

The following method for the estimation of citric and tartaric acid, free or combined, is given by E. Fleischer (*Arch. Pharm.* [3], v. 97):—

1. *When the two Acids are present in a liquid in the free state or combined with Alkalis.*—The solution, if necessary, is acidified with acetic acid, and potassium acetate is added in excess, together with an amount of alcohol of 95° equal to twice the volume of liquid operated upon; after an hour's standing the precipitate of potassium tartrate is filtered off and dissolved in hot water; and the acid is estimated by means of standard soda or ammonia solution. To the filtrate from the precipitated potassium tartrate a solution of basic lead acetate is added; the precipitate of lead citrate is collected, after a while, on a filter, washed with a mixture of equal volumes of alcohol and water, and removed to a beaker, in which it is suspended in water; and sulphuretted hydrogen is passed through this mixture. When the lead is completely removed, the liquid is filtered, boiled to expel sulphuretted hydrogen, and titrated with soda-solution. This method is applicable in the presence of metals which are precipitated by sulphuretted hydrogen from an acid solution, provided that no acid but acetic (in addition to the two to be estimated) be present.

2. *When Acids other than Acetic, and Bases other than the Alkalis, are present, but only such bases as form soluble compounds with the acids present.*—If metals precipitable by sulphuretted hydrogen are present, these are removed (zinc, after addition of sodium acetate), the precipitated sulphides being washed with hot water containing a little acetic acid; to the filtrate excess of lead acetate is added; the precipitate, after being washed with a mixture of 2 vols. of alcohol and 1 vol. of water, is removed to a beaker; and ammonia (free from carbonate) is added. The solution, which now contains lead tartrate and citrate, is separated from the insoluble part (which is washed with dilute ammonia). To the filtrate ammonium sulphide is added, then a little acetic acid, and the liquid is boiled until all sulphuretted hydrogen is removed. After filtering off the precipitated lead sulphide, potassium acetate and two volumes of alcohol are added to the filtrate, and the precipitate of potassium tartrate is treated as already described. In the filtrate citric acid is estimated as above; but if the original liquid contained hydrochloric acid, a small quantity of this acid will be found in this filtrate, in which case calcium chloride is added to the alcoholic liquid, followed by the addition of ammonia; the precipitate of calcium citrate is collected, washed with alcohol, and dissolved in acetic acid; and the liquid is precipitated with lead acetate. The rest of the process is the same as that already described.

3. *When Lime and Phosphoric acid, besides the foregoing Bases and Acids, are present.*—After the removal of the metals precipitable by sulphuretted hydrogen, ammonium acetate in excess is added to the filtrate, which is heated to boiling and filtered, and the filtrate, when cold, is precipitated with lead acetate; this precipitate is treated with ammonia, whereupon lead citrate and tartrate pass into solution; the remainder of the process is the same as that before described.

That part of the precipitate by lead acetate which is insoluble in ammonia, is treated with caustic soda, ammonium sulphide is added, then a small quantity of acetic acid, and the liquid is boiled and filtered. The filtrate is divided into three portions; in one part sulphuric acid is estimated, in another oxalic acid, and in the third phosphoric acid.

Estimation of Tartaric and Citric acids in the Juice of Fruits.—The juice, after being clarified as far as possible, is precipitated with lead acetate; the precipitate is collected, washed with aqueous alcohol, treated with excess of ammonia, and again

filtered; ammonium sulphide is added, then lead acetate; and the precipitated lead sulphide is removed by filtration. Tartaric acid is removed as potassium tartrate; calcium chloride and ammonia are added—together with a little alcohol—to the filtrate; the precipitate is washed with boiling lime-water in order to remove calcium malate; the residue is then dissolved in acetic acid; the liquid is precipitated with lead acetate; and the citric acid estimated as already described.

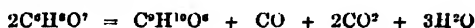
Estimation of the Two Acids in Insoluble Substances.—Crudo argol is boiled in dilute nitric acid. Ammonium oxalate is added in excess, and the liquid filtered while hot; to the filtrate potassium acetate and alcohol are added. To determine the citric acid in calcium citrate, the substance is dissolved in acetic acid, precipitated with lead acetate, and the acid estimated in this precipitate. If both acids are present as calcium salts, the substance is dissolved in nitric acid, the solution precipitated with lead acetate, and the precipitate treated as already described.

A method of estimating the amount of tartaric acid in commercial citric acid, agreeing essentially with that of Fleischer, is given by A. H. Allen (*Pharm. J. Trans.* [3], vi. 6; *Jahresh.* 1875, 968).

On the Adulterations and Impurities of Citric and Tartaric Acids, and on the precautions to be observed in testing for these acids by means of a potassium salt, see A. H. Allen (*Chem. News*, 1875, xxxii. 277).

Action of Sodium on Citric acid.—Kämmerer, by treating an alcoholic solution of dehydrated citric acid with sodium, obtained a product which he regarded as hydro-citric acid, $C^6H^9O^7$ (1st Suppl. 473). According to Claus, however (*Deut. Chem. Ges. Ber.* viii. 155), this supposed acid has no existence. When sodium acts on citric acid in the manner just mentioned, no hydrogen is added on to the citric acid, the quantity evolved as gas being equivalent to that of the sodium dissolved, and the whole of the citric acid originally present in the solution being recoverable from it after the action is over. Kämmerer's so-called hydrocitric acid was, in fact, nothing but citric acid.

Action of Hydrochloric acid.—Citric acid heated with concentrated hydrochloric acid to 140° – 150° partly becomes syrupy and non-crystallisable, and is partly converted into aconitic acid, and at 190° – 200° into diconic acid, $C^6H^{10}O^6$, with separation of carbon monoxide and dioxide:



(Hergt, *J. für Chem.* [2], viii. 372).

Citrates. *Normal bismuth citrate*, $C^6H^8O^7Bi$, is obtained by heating 10 pts. basic bismuth nitrate, with 7 pts. crystallised citric acid, and 30–40 pts. water for a few minutes, till a drop of the mixture mixed with aqueous ammonia forms a clear solution. The crystalline mass is then to be treated with 8 or 10 times its bulk of water, the solution decanted after some time, the crystalline precipitate washed 3 or 4 times in a similar manner, and then dried. On dissolving this salt at a gentle heat in aqueous ammonia, and leaving the solution to cool, a crystalline mass is obtained, which has the composition $C^6H^8O^7Bi + 3NH^4OH = C^6H^8O^7(NH^4)^3Bi(OH)^3$, and retains its solubility in water after drying over the water-bath.

Normal ferric citrate unites with ammonia in like manner, forming the salt $C^6H^8O^7(NH^4)^3Fe(OH)^3$. In addition to the green normal ammonio-ferric citrate, $(C^6H^8O^7)^2Fe(NH^4)^3$, there are also two acid double salts, viz. $(C^6H^8O^7)^2Fe(NH^4)^2H$ and $(C^6H^8O^7)^2Fe(NH^4)H^2$, which are likewise green. With excess of ammonia all three give brown solutions, which recover their green colour but slowly when treated with citric acid. By acting on normal ferric citrate with the salt $C^6H^8O^7(NH^4)^3Bi(OH)^3$, the double salt $(C^6H^8O^7)^2Fe(NH^4)^3Bi(OH)^3$ is formed, the light green solution of which remains clear when acidulated with citric or with nitric acid (R. Rother, *Pharm. J. Trans.* [3], vi. 764).

Citric Ethers (Hunäus, *Deut. Chem. Ges. Ber.* ix. 1749). *Trimethyllic citrate*, $C^6H^9(CH^3)^3O^7$ —produced, together with the two acid ethers, which are difficult to separate from it, by saturating a solution of citric acid in methyl alcohol with hydrochloric acid gas (i. 1001)—forms hard crusts, like milk-sugar, and separates from dilute solutions in well-defined triclinic crystals melting at 78.5° – 79° . It boils at 283° – 287° , and is at the same time partly resolved into water and trimethyllic aconitate, $C^6H^9(CH^3)^3O^6$, boiling at 270° – 271° . By boiling trimethyllic citrate with a quantity of potash not sufficient for its complete decomposition, no salt of either of the acid citric ethers is formed, but a portion of the neutral ether is converted into neutral potassium citrate.

Phosphorus pentachloride converts trimethyllic citrate into trimethyllic monochlorotricarballylate, $C^6H^9ClO^6 = C^6H^9Cl(CO.OQH)^3$, which separates, on pouring the product of the reaction into ice-cold water, as a thick colourless oil, and is resolved by heat into hydrochloric acid and trimethyllic aconitate.

Sodium acts strongly on trimethyl citrate; but the product treated with ethyl bromide yields nothing but sodium bromide and resinous products.

Trimethyl Acetyl citrate, $C^{11}H^{10}O^8 = C^3H^4(\odot C^2H^3O)(COOCH^3)^3$, obtained by heating trimethyl citrate on the water-bath with 1 mol. acetyl chloride, is a colourless liquid boiling at $280^\circ-282^\circ$. On boiling it with 1 mol. sodium ethylate and absolute alcohol, sodium acetate separates out, and the filtrate when evaporated leaves a viscid uncrystallisable mass, yielding by saponification nothing but acetic acid (Hunäb.).

Ethyl Citrates (Claus n. Roennsfahrt, *Deut. Chem. Ges. Ber.* viii. 866). Triethyl citrate, if perfectly anhydrous, is not acted upon by sodium-amalgam, even if it be diluted with ether; but on adding water by drops, a reaction is set up, resulting, however, not in the reduction of the citric acid, but in the replacement of one ethyl-group after another by sodium, according to the quantity of water added. When the reaction is over, it is best to add ether, separate the mercury, and agitate the turbid ethereal solution with an equal volume of water. The unaltered neutral citric ether then remains in the ethereal layer, and the sodium salts of citric, monethylcitric, and diethylcitric acids pass into the aqueous solution. This solution is to be evaporated to dryness, and the residue exhausted with strong alcohol, which dissolves the whole of the sodium diethylcitrate, and part of the less soluble monethylcitrate, these salts being afterwards separated by their different solubilities in alcohol. The residue, insoluble in alcohol, is dissolved in water; and the citric acid is precipitated by lead nitrate, the easily soluble monethylcitrate of lead then remaining in solution.

Monethylcitric acid, $C^6H^7(C^2H^3)O^7 = C^3H^4(OC^2H^3)(CO^2H)^3$, crystallises in fan-shaped groups of thin prisms with truncated end-faces. It dissolves easily in alcohol and ether, and when boiled with excess of potash-ley yields a distillate which distinctly exhibits Lieben's alcohol reaction (production of iodoform by heating with iodine and potash, 1st Suppl. 593). The *sodium salt* forms transparent, mostly well-defined prisms, which easily deliquesce when exposed to the air, and are extremely soluble in water. The solution is not precipitated by barium chloride or lead acetate, but on heating it with caustic baryta, alcohol is formed, and barium citrate separates out. The *silver salt* dissolves readily in water, and may be crystallised therefrom, without much decomposition, in rhombic tablets. By prolonged boiling the silver is reduced, but not in specular form. The *barium salt* (steplike groups of crystals) and the *lead salt* (an indistinctly crystalline mass) are very soluble in water, and decompose at 100° , with formation of alcohol and citric acid.

Diethylcitric acid, $C^6H^8(OC^2H^3)^2(CO^2H)^3$, appears to be uncrystallisable. Its *sodium salt* is deliquescent and easily soluble in alcohol. The *barium* and *lead salts* are easily soluble hygroscopic syrupy masses, which by prolonged heating at 100° are resolved into alcohol and the corresponding citrates.

Chlorocitric acid, $C^6H^7ClO^8$, is obtained, not directly from citric acid, but by the action of hypochlorous acid on acetic acid in aqueous solution. It is soluble in water and in ether, uncrystallisable, and has consequently not yet been obtained pure. It is easily decomposable, and when heated with water yields hydrochloric acid and oxycitric acid. When impure chlorocitric acid (still containing acetic acid) is subjected to the reducing action of zinc and hydrochloric acid, a crystallisable product is formed, which appears to be a mixture of citric and tricarballic acids (Fawcett, *Liebig's Annalen*, clxxviii. 150).

Oxycitric acid, $C^6H^8O^8 = C^3H^4(OH)(CO^2H)^3$ (Fawcett, *loc. cit.*) Formed, as just mentioned, by decomposition of chlorocitric acid. It is prepared by dissolving 174 grams of acetic acid in a liter of water, adding sodium carbonate until the solution is slightly alkaline, and then a liter of hypochlorous acid containing 55 grams of $HClO$. When the smell of hypochlorous acid has disappeared, the required quantity of hydrochloric acid is added, the solution is evaporated, and the residue exhausted with ether-alcohol, which is distilled off. The residue is then dissolved in water, and the solution heated with milk of lime until the bulky precipitate becomes granular. The calcium salt is decomposed with sulphuric acid, the free acid dissolved in alcohol, and after the excess of sulphuric acid has been removed by baryta, the alcohol is evaporated, and the dark residue purified by precipitating its solution with lead acetate, and decomposing the lead salt with hydrogen sulphide.

Oxycitric acid does not crystallise, but forms a viscid deliquescent mass, having an agreeable sour taste. It is a tribasic acid—that is to say, it contains three carboxyl groups CO^2H ; but, like citric acid and other similar acids, it can also form tetrametallic salts by substitution of a metal for hydrogen in one of the alcoholic hydroxyls. The oxy-citrates of alkali-metal do not crystallise.

The *calcium salt*, $(C^3H^4O^7)Ca^2 + 9H^2O$, is a bulky amorphous precipitate, which on heating changes into microscopic needles, and dissolves readily in dilute acetic acid.

The *barium salt*, $(C^3H^4O^7)Ba^2 + 5H^2O$, is an amorphous white powder, which when heated with water becomes granular, and is even less soluble than the calcium salt.

The *cadmium salt*, $(C^3H^4O^7)Cd^2 + 6H^2O$, behaves like the other salts, the amorphous precipitate changing on heating (very quickly at 130°) into microscopic, transparent, rhombic plates.

The *copper salt*, $(C^3H^4O^7)Cu^2 + xH^2O$, is very freely soluble in water, and does not crystallise. Alcohol precipitates it as a $\frac{1}{2}$.

The *ethyl ether*, $C^3H^4O^7(C^2H^5)^2$, is obtained by the action of hydrochloric acid on an alcoholic solution of the acid. It is a dark yellow oil having a very bitter taste.

Nitrocitric acid, $C^3H^3(NO^2)O^7$ (Champion a. Pellet, *Bull. Soc. Chim.* [2], xxiv. 448). This acid is formed by gradually adding dehydrated citric acid to a mixture of 1 pt. fuming nitric acid and 2 pts. sulphuric acid. If the solution is concentrated, the nitro-acid separates in crystals after a few days. The mixture is poured into an excess of water, rise of temperature being avoided; the sulphuric acid is removed by barium carbonate; the filtrate saturated with alkaline carbonate and precipitated by excess of triplumbic acetate; and the washed precipitate is decomposed by hydrogen sulphide. Or the solution, after being freed from sulphuric acid, is saturated with baryta, whereby a precipitate of nitrocitrate and nitrate of barium is produced; the latter salt is removed by washing with water, and the nitrocitrate is decomposed by the exact quantity of sulphuric acid required to remove the barium.

Solutions of nitrocitric acid must not be too much concentrated by evaporation, or they will decompose even in a vacuum. The acid is insoluble in ether, but alcohol dissolves it in all proportions. The *alkali salts* are crystallisable. The *barium salt* has the composition $[C^3H^3(NO^2)O^7]Ba^2$; the *lead salt* $[C^3H^3(NO^2)O^7]Pb^2$.

PYROCITRIC ACIDS, $C^3H^3O^7$.

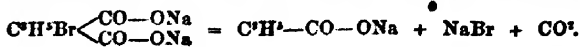
Formation.—The normal product of the decomposition of aconitic acid by heat is itaconic acid; all other products obtained in the dry distillation of citric acid are formed by secondary reactions. At very high temperatures, or after prolonged heating, the chief product is citraconic anhydride, which, indeed, has long been known to result from the action of heat on citraconic and itaconic acids (i. 994); mesaconic acid undergoes the same decomposition at its boiling point (250°). On the other hand, a temperature of 100° – 175° appears to be favourable to the formation of itaconic acid, as in Willm's process for preparing that acid from citraconic acid (1st Suppl. 780). When, however, a concentrated solution of itaconic or citraconic acid is heated to 180° – 200° , the liquid is found to contain a considerable quantity of mesaconic acid, carbon dioxide and an empyreumatic oil being formed at the same time (Th. Swarts, *Bull. Acad. Royale Belgique* [2], xxxvi. No. 7 [1873]).

Electrolysis.—When a solution of potassium citraconate is subjected to the action of the voltaic current, carbon dioxide is given off at the positive pole, together with ordinary allylene, $CH^2=C=CH$; which precipitates silver and copper solutions. The electrolysed liquid appears to contain acrylic and mesaconic acids. Mesaconic acid likewise yields by electrolysis an allylene which precipitates silver solution, the other products being apparently itaconic and acrylic acids. Itaconic acid, on the other hand, yields β -allylene or allene, $CH^2=C=CH^2$ (p. 62), which does not precipitate silver or copper solutions (Aarland, *J. pr. Chem.* [2], vii. 142, 145).

Action of Zinc-dust.—Citra-, ita-, and mesaconic acids, subjected in alcoholic solution to the action of zinc-dust, are converted into ordinary pyrotartaric acid, itaconic acid less quickly than the other two acids. The same transformation is effected by sodium-amalgam (Böttlinger, *Deut. Chem. Ges. Ber.* ix. 1821).

Addition-products and Constitution of the Pyrocitric Acids (Fittig, *Liebig's Annalen*, cxxxvii. 42; *Deut. Chem. Ges. Ber.* x. 513).

Citraconic acid and its anhydride dissolve readily in fuming hydrobromic acid, and in the course of a few days are converted into hard, shining monoclinic crystals of citra-bromopyrotartaric acid melting at 148° . On prolonged boiling of its aqueous solution, this substance gives off the whole of its bromine as hydrogen bromide, and is resolved into methacrylic and mesaconic acids: in alkaline solution, it is decomposed much more rapidly on warming, yielding almost exclusively methacrylic acid:



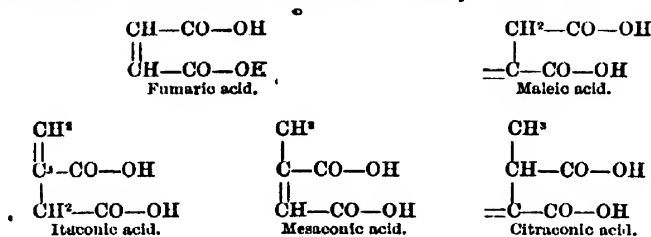
This decomposition of citrabromopyrotartaric acid affords the best means of preparing methacrylic acid, which may thus be easily obtained in large quantity.

Itaconic acid does not dissolve in fuming hydrobromic acid, but when finely pulverised and left in contact with the acid for some days, with occasional agitation, it is completely converted into hard monoclinic crystals of itabromopyrotartaric acid, differing in form from those of citrabromopyrotartaric acid, melting at 137° , decomposed by prolonged boiling with water, or by once boiling with solution of sodium carbonate.

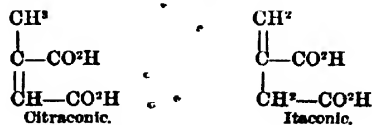
Mesaconic acid, like fumaric acid, is not attacked by hydrobromic acid at ordinary temperatures, but by prolonged heating with water at 100° or 140° , it is converted into a bromotartaric acid identical with that which is produced from citraconic acid at ordinary temperatures.

Similar differences are observed in the behaviour of these acids with bromine—citraconic acid uniting with that element very readily at ordinary temperatures, mesaconic acid only on warming. Both the dibromopyrotartaric acids $C^2H^2O^2Br^2$ thus obtained crystallise easily; that from citraconic acid melts at 150° ; that from mesaconic acid at 170° . By prolonged boiling with water they are resolved into carbon dioxide, hydrogen bromide, and bromomethacrylic acid.

In their behaviour to bromine, hydrobromic acid, and nascent hydrogen, the pyrocitric acids resemble maleic and fumaric acids, yielding with hydrogen identical products, with bromine isomeric products, and with hydrobromic acid either isomeric or identical products, according to the manner in which the atoms of the hydracid are attached. Moreover, citraconic acid resembles maleic acid in the facility with which it forms addition-products at ordinary temperatures, whereas itaconic and mesaconic acids—especially the latter—resemble fumaric acid in requiring the aid of heat to enable the addition to take place. For this reason Fittig regards maleic and citraconic acid as compounds in which the combining capacities of the carbon atoms are not fully satisfied; fumaric, itaconic, and mesaconic acids, on the other hand, as compounds in which two of the carbon atoms are doubly linked; thus—



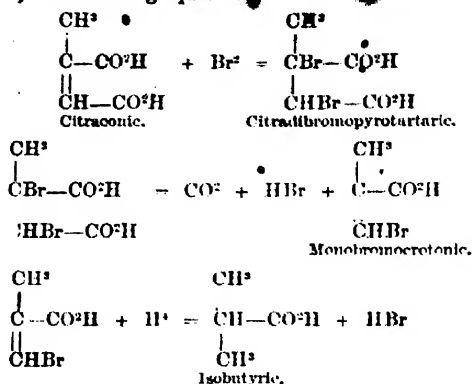
Meilly, on the other hand (*Liebig's Annalen*, clxxi. 181), represents citraconic as well as itaconic acid by a formula containing a pair of doubly linked carbon-atoms; thus—



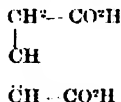
These formulæ readily account for the formation of the two isomeric allylenes by electrolysis of these two acids (p. 62). Citraconic acid, subjected to electrolysis, yields, by elimination of 2CO^2 and 2H , ordinary allylene $\text{CH}^2-\text{C}\equiv\text{CH}$; and itaconic acid, in like manner, yields β -allylene or allene $\text{CH}^2=\text{C}=\text{CH}^2$. An acid constructed according to Fittig's formula of citraconic acid could not yield ordinary allylene except by transference of a hydrogen-atom from the middle to the end carbon-atom.

Meilly's formula for citraconic acid is further supported by the fact observed by Swarts, that the bromocrotonic acid obtained from citradibromotartaric acid is converted by the action of sodium-amalgam into isobutyric acid. Hence it appears that two acids with similar carbon structure, like itaconic and citraconic acids ($\text{C}-\text{C}\equiv\text{C}$), can yield by separation of an atom of carbon, in the one case, an acid with normal carbon-linking (succinic acid from itaconic acid through the medium of aconic acid, *2nd Suppl.* 22), in the other an acid with branched carbon-linking (isobutyric acid

from citraconic acid through the medium of citradibromopyrotartaric acid). This last result is explained by the following equations:—



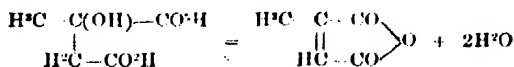
L. Henry (*Bull. Soc. Chim.* [2], xxiii. 347) formulates citraconic and itaconic acids in the same way as Meilly, and represents mesaconic acid by the formula



This acid when electrolysed yields ordinary allylene, a hydrogen-atom being transferred from the middle CH-group to the CH^3 -group.

Morawski (*J. pr. Chem.* [2], xii. 396) regards this formula of mesaconic acid as inadmissible, on the ground that the bromocrotonic acid, $\text{C}^3\text{H}^3\text{BrO}^2$, obtained from mesadibromopyrotartaric acid is converted by sodium-amalgam, like that obtained from the corresponding citra-compound, into isobutyric acid, and is therefore probably identical with the latter. Moreover, the formation of one and the same crotonic (methacrylic) acid from citraconic and from mesaconic acid, and the production of chlorocitraconic acid by the action of chlorine on mesaconic acid, lead to the conclusion that mesaconic acid, as well as citraconic acid, contains a methyl-group.

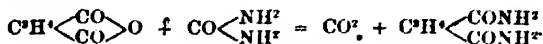
Citraconic Acid and Anhydride. Citraconic anhydride is formed, together with pseudopropyl alcohol and a small quantity of pseudopropyl citraconate, by the dry distillation of oxypyrotartaric acid. Its formation is represented by the equation:—



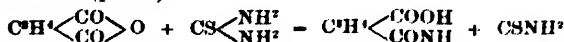
(Demarcay, *Compt. rend.* lxxxii. 1337).

When citraconic anhydride, $\text{C}^3\text{H}^3\text{O}^2$, is gently heated in a retort, it begins to evolve carbon dioxide at 180° , and on continuing the heating till the temperature gradually rises to 190° , the contents of the retort become converted into a brown very viscid mass, which, when distilled, first yields a small quantity of citraconic anhydride, and afterwards, at 220° – 270° , a brown oil insoluble in water, a carbonaceous residue being left in the retort. The brown oil distilled with water yields a distillate of xeronic anhydride, $\text{C}^3\text{H}^3\text{O}^2$ (Fittig, *Ber.* ix. 1189). See Xeronic Acid.

Citraconic anhydride heated to 115° with carbamide (urea) yields carbon dioxide and citraconamide:



With thiocarbamide at 130° , on the other hand, the product consists of citraconthiocarbamic acid (p. 387):



Action of Chlorine on Sodium Citraconate.—When chlorine is allowed to act for several days on sodium citraconate, chlorocitraconic acid (p. 515) is formed,
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together with a heavy yellowish green oil consisting chiefly of a mixture of trichlorobutyric acid and an indifferent substance of penetrating odour; a further quantity of this oil is obtained by adding hydrochloric acid to the aqueous supernatant liquor and heating in a retort to 100° , whereupon a distillate of water and the oil slowly passes over. By neutralising with soda and treating with ether, the indifferent body is removed, and by acidulating the sodium salt and distilling, the trichlorobutyric acid is obtained as a yellowish oil from which the pure acid is obtained by careful distillation at a low temperature and concentrated sulphuric acid; addition of a fragment of acid already crystallised to the remaining oil causes it to crystallise, the crystals melting at 50° . Even at this temperature it volatilises, subliming in glistening needles if the atmosphere is free from moisture; at 140° – 146° it becomes yellow, and evolves bubbles of gas. The ammonium and lead salts crystallise well. Heated to 100° with strong bases the acid is resolved into hydrochloric and dichlorocrotonic acids, $\text{C}^3\text{H}^3\text{Cl}^2\text{O}^2 = \text{HCl} + \text{C}^2\text{H}^2\text{Cl}^2\text{O}^2$. The dichlorocrotonic acid thus obtained is volatile, crystallises by sublimation, or from a hot aqueous solution in long needles, and melts at a gentle heat (Gottlieb, *J. pr. Chem.* [2], xii. 1).

The action of chlorine on sodium citraconate has been further studied by Morawski (*ibid.* xii. 369), who finds that the formation of trichlorobutyric acid is independent of that of the indifferent oil, since the solution of sodium citraconate saturated with chlorine to a certain degree, yields, on addition of hydrochloric acid, an oily precipitate of pure trichlorobutyric acid completely soluble in aqueous sodium carbonate. The production of trichlorobutyric acid is due to the previous formation of monochlorocrotonic acid, which is converted into trichlorobutyric acid by addition of 1 mol. chlorine. The monochlorocrotonic acid may in fact be isolated by arresting the action of the chlorine at a certain stage, and separates in slender silky needles melting at 58.5° ; it is identical with that which Gottlieb obtained by acting on the same trichlorobutyric acid with zinc-dust and hydrochloric acid (see Crotonic acids), and is formed by decomposition of citradichloropyrotartaric acid, which is the first product of the action of chlorine on sodium citraconate.

The indifferent oil which is usually formed together with the trichlorobutyric acid, consists mainly of trichloroacetone, if the action of the chlorine has been carried far enough; in the contrary case lower chloroacetones are formed. The trichloroacetone thus obtained is reduced by sodium-amalgam to acetone, and is resolved by treatment with the calculated quantity of barium hydrate into acetic acid and chloroform:



According to the last reaction, it is identical with the trichloroacetone which Krämer obtained by the action of chlorine on the mixed products formed by oxidising commercial isobutyl alcohol with chromic acid mixture (p. 25). It is a colourless very mobile oil, the odour of which is not unpleasant, but becomes sharply pungent on heating. It is not quite insoluble in water, but the solution becomes turbid on the heat of the hand. In thin layers it volatilises at ordinary temperatures. It dissolves in strong hydrochloric acid, and separates unaltered on dilution.

The series of actions taking place when chlorine is passed into a solution of sodium citraconate may be represented by the following equations:

- (1.) $\text{C}^3\text{H}^4\text{Na}^2\text{O}^4 + \text{Cl}^2 = \text{C}^3\text{H}^3\text{Na}^2\text{ClO}^4$
Sodium Citraconate, Sodium citradichloropyrotartarate.
- (2.) $\text{C}^3\text{H}^4\text{Na}^2\text{ClO}^4 = \text{C}^2\text{H}^3\text{NaClO}^3 + \text{NaCl} + \text{CO}^2$
Citradichloropyrotartarate, Monochlorocrotonate.
- (3.) $\text{C}^3\text{H}^4\text{Na}^2\text{ClO}^4 + \text{H}^2\text{O} = \text{NaCl} + \text{C}^2\text{H}^3\text{NaClO}^3$
Citradichloropyrotartarate, Acid monochlorocitraconate.
- (4.) $\text{C}^2\text{H}^3\text{NaClO}^3 + \text{C}^2\text{H}^3\text{NaClO}^3 = \text{C}^2\text{H}^2\text{ClO}^2 + \text{C}^2\text{H}^2\text{Na}^2\text{ClO}^3$
Chlorocrotonate, Acid chlorocitraconate, Chlorocrotonic acid, Chlorocitraconate.
- (5.) $\text{C}^2\text{H}^2\text{ClO}^2 + \text{Cl}^2 = \text{C}^2\text{H}^2\text{Cl}^2\text{O}^2$
Chlorocrotonic acid, Trichlorobutyric acid.
- (6.) $\text{C}^2\text{H}^3\text{Na}^2\text{ClO}^3 + \text{Cl}^2 = \text{C}^2\text{H}^2\text{ClO} + 2\text{NaCl} + 2\text{CO}^2$
Chlorocitraconate, Monochloroacetone.
- (7.) $\text{C}^2\text{H}^2\text{ClO} + \text{Cl}^2 = \text{C}^2\text{H}^2\text{Cl}^2\text{O} + 2\text{HCl}$
Monochloroacetone, Trichloroacetone.

Chlorocitraconic Anhydride, $\text{C}^3\text{H}^2\text{ClO}^4$, is formed, together with water, by the action of heat on chlorocitramalic acid, and is most conveniently prepared by heating 20–30 grams of that acid in a retort placed in an air-bath. The anhydride then sublimes in the neck of the retort, and may be taken out from time to time, freed by exposure to the air from small quantities of a strongly-smelling substance which adheres to it, and purified by repeated sublimation.

Chlorocitraconic anhydride crystallises, like the corresponding bromine-compound, and *Benzil* in shining, colourless, crystalline laminae. It has an agreeable aromatic odour, melts at 100° , sublimes at a lower temperature, and gradually disappears on exposure to the air. It dissolves very slowly in cold, more quickly in hot water, being converted thereby into the acid, easily in alcohol and in ether. On evaporating the aqueous solution, the acid volatilises almost completely with the aqueous vapour, so that very little of the anhydride is left. The ethereal solution, on the other hand, leaves on evaporation an oil, which when touched solidifies to the crystalline anhydride.

Chlorocitraconic acid, $\text{C}^3\text{H}^2\text{ClO}^4$, is not known in the solid state; it is converted by nascent hydrogen into pyrotartaric acid, $\text{C}^3\text{H}^2\text{O}^4$.

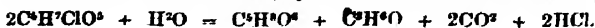
The metallic chlorocitraconates are not decomposed by boiling with water, or during the evaporation of their aqueous solutions. The *ammonium salt* is easily soluble in water, and crystallises in needles. The *sodium salt* is very easily soluble, and crystallises only from very concentrated solutions. The *barium salt*, $\text{C}^3\text{H}^2\text{ClO}^4\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$, is obtained as a precipitate sparingly soluble in water; it dissolves in aqueous chlorocitraconic acid, forming an acid salt which crystallises in shining needles. The *calcium salt*, $\text{C}^3\text{H}^2\text{ClO}^4\text{Ca}$, forms microscopic nodules slightly soluble in water, less soluble in alcohol. The *lead salt*, $\text{C}^3\text{H}^2\text{ClO}^4\text{Pb}$, is a white amorphous precipitate. The *silver salt*, $\text{C}^3\text{H}^2\text{ClO}^4\text{Ag}^2$, is slightly soluble in cold, easily in hot water, and separates from this solution in small crystals. It dissolves also in the aqueous acid, and is thereby converted into an acid salt, $\text{C}^3\text{H}^2\text{ClO}^4\text{Ag}$, which crystallises in shining colourless prisms, more soluble than the neutral salt (Gottlieb, *J. pr. Chem.* [2], vii. 78; Swarts, *Bull. Acad. royal. Belgique* [2], xxxiii. no. 1 [1872]).

Citramalic Acid, $\text{C}^3\text{H}^4\text{O}^5$. This acid, homologous with malic acid, was discovered by Carius, who obtained it by the action of zinc on an aqueous solution of chlorocitramalic acid, $\text{C}^3\text{H}^2\text{ClO}^4$, the product of the action of hypochlorous acid on citraconic acid: $\text{C}^3\text{H}^2\text{O}^4 + \text{HClO} = \text{C}^3\text{H}^2\text{ClO}^4$ (1st Suppl. 471), or of chlorine on sodium citraconate (see last page). A 10 per cent. solution of the chlorinated acid is heated with metallic zinc as long as gas continues to escape, then neutralised with ammonia and precipitated by lead acetate, and the well-washed precipitate is decomposed by hydrogen sulphide. The filtrate, after decolorisation by animal charcoal, leaves pure citramalic acid (Carius, *Ann. Ch. Pharm.* cxxix. 164). This acid is also the action of hydriodic acid on oxycitraconic acid, $\text{C}^3\text{H}^2\text{O}^5$ (Morawsky, *J. pr. Chem.* [2], xi. 69).

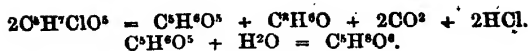
Citramalic acid forms an amorphous deliquescent mass, which melts above 100° , and is decomposed by dry distillation. It is bibasic. The *ammonium salt*, $\text{C}^3\text{H}^4\text{O}^5(\text{NH}^4)^2$, and the *potassium salts*, $\text{C}^3\text{H}^4\text{O}^5\text{K}^2$, are crystallisable, and melt in their water of crystallisation when heated. The *barium salt*, $\text{C}^3\text{H}^4\text{O}^5\text{Ba} + \text{H}_2\text{O}$ (at 100°), dissolves sparingly in cold, freely in boiling water, and in the free acid, and forms soluble double salts with the salts of the alkali-metals. The *lead salt*, $\text{C}^3\text{H}^4\text{O}^5\text{Pb}$, is obtained by precipitation in white flocks, which become granular when boiled with the liquid. The *silver salt*, obtained by precipitation of the cold solutions, is amorphous, dissolves in water at 60° , crystallises on cooling, and is decomposed on heating the solution above 60° .

Chlorocitramalic acid, $\text{C}^3\text{H}^2\text{ClO}^4$, forms shining rhombic crystals, easily soluble in water, alcohol, and ether, melts and partly volatilises at about 100° , solidifies on cooling to an amorphous mass, and distils with partial decomposition at a higher temperature. It is a bibasic acid. The *neutral potassium salt*, $\text{C}^3\text{H}^2\text{ClO}^4\text{K}^2$, is crystallisable, the *silver salt*, $\text{C}^3\text{H}^2\text{ClO}^4\text{Ag}^2$, separates on treating the free acid with silver acetate in white dendritic crystals which decompose easily when heated, with formation of silver chloride.

Chlorocitramalic acid heated with water in a sealed tube, is resolved into citratartaric acid, $\text{C}^3\text{H}^2\text{O}^5$, carbon dioxide, hydrochloric acid, and acetone:



Oxycitraconic Acid, $\text{C}^3\text{H}^2\text{O}^5$ (Morawsky, *J. pr. Chem.* [2], x. 79; xi. 430). This acid is formed, together with citratartaric acid, $\text{C}^3\text{H}^2\text{O}^5$, and acetone, when chlorocitramalic acid, its barium salt, or its ethylic ether, is boiled with excess of tartaric acid:



To prepare oxycitraconic acid, monochlorocitramalic acid is dissolved in boiling water, excess of baryta-water is added, and the liquid is boiled as long as carbon dioxide continues to escape, then quickly filtered. On cooling, it solidifies to a pulp consisting of needle-shaped crystals of barium oxycitraconate, which may be collected on a filter and washed with cold water. By decomposing this salt with hydrochloric acid, and agitating with ether, the free acid is obtained as a colourless crystalline mass.

Oxycitraconic acid crystallises from water in beautiful prisms, which dissolve very easily in water, alcohol, and ether. It does not lose weight at 100° , but softens at 120° – 130° , and swells up to a spongy mass (citratartaric anhydride?), the aqueous solution of which exhibits all the reactions of citratartaric acid. Oxycitraconic acid is also converted into citratartaric acid by heating it with water to 110° – 120° . It does not react with bromine or with sodium-amalgam, but when heated to 100° – 110° in sealed tubes with excess of concentrated hydriodic acid, it is converted into citramalic acid (p. 515). Oxycitraconic acid unites with hydrochloric acid, forming hydrochloroxy citraconic acid, $\text{C}^3\text{H}^3\text{ClO}^3$, isomeric with chlorocitramalic acid.

Oxycitraconic acid is bibasic, forming acid and neutral salts. The neutral oxycitraconates of the alkali-metals dry up over oil of vitriol to tenacious masses, and are gradually precipitated from their aqueous solutions by alcohol in viscid drops. The neutral ammonium salt, $\text{C}^3\text{H}^3(\text{NH}^4)^2\text{O}^3$, crystallises, after prolonged standing over sulphuric acid, in radiate groups of needles. The acid ammonium salt, $\text{C}^3\text{H}^3(\text{NH}^4)\text{O}^3$, forms microscopic prisms, often with re-entering angles. The acid potassium salt forms microscopic prisms less soluble than the free acid. The neutral barium salt, $\text{C}^3\text{H}^3\text{BaO}^3 + 4\text{H}_2\text{O}$, forms shining needles, freely soluble in hot, nearly insoluble in cold water; gives off its water over sulphuric acid. It is not decomposed by boiling for a day with water, but when heated with water to 120° it yields first citratartarate of barium, then carbon dioxide and an oily body. The neutral strontium salt, $\text{C}^3\text{H}^3\text{SrO}^3 + 4\text{H}_2\text{O}$, resembles the barium salt, but is more soluble. The calcium salt is very soluble, crystallises in microscopic flattened pyramids, and is precipitated from aqueous solution by alcohol as a granular powder. The magnesium, cadmium, cobalt, and uranium salts, dry up to gummy masses. The lead salt, $2\text{C}^3\text{H}^3\text{PbO}^3 + 9\text{H}_2\text{O}$, forms silky, very sparingly soluble needles, which give off $8\text{H}_2\text{O}$ over sulphuric acid or at 100° , and begin to decompose at 120° . It cannot be recrystallised from water, as it is thereby partially decomposed. Heated with water to 120° , it is converted into citratartarate. The silver salt is a white precipitate, which very quickly turns brown, and when boiled with water is immediately decomposed, with separation of metallic silver (distinction from citratartaric acid). The mercurous salt is a white precipitate which, when boiled with the liquid, turns grey and partly disappears.

With ferric chloride, neutral potassium oxycitraconate forms a reddish-brown precipitate, which dissolves in excess of either reagent, and when boiled with the liquid containing ferric chloride, disappears completely, with evolution of carbon dioxide and a pungent vapour which does not redden litmus, the liquid at the same time turning bluish-green, and being afterwards found to contain ferrous oxide. If the precipitate be boiled after washing with water, the decomposition-phenomena are less marked, and only traces of ferrous oxide are produced. With ferrous sulphate sodium oxycitraconate does not form any precipitate at ordinary temperatures, but on boiling the liquid, a dark-coloured precipitate is formed, with evolution of carbon dioxide. With chromic sulphate, a whitish-green precipitate is formed, which likewise disappears on boiling, with evolution of carbon dioxide.

Alkaline oxycitraconates do not form precipitates with salts of aluminium, manganese, cobalt, or nickel.

Hydrochloroxy citraconic acid, $\text{C}^3\text{H}^3\text{ClO}^3$, isomeric with chlorocitramalic acid, is obtained by heating oxycitraconic and fuming hydrochloric acid together to 100° – 110° for an hour in sealed tubes. The nearly colourless liquid thereby produced deposits the hydrochloroxy citraconic acid after a while in thin nacreous rhombic laminae.

Hydrochloroxy citraconic acid is easily soluble in water, and crystallises therefrom with unusual facility in fine rhombic tables. It is very soluble also in ether. It melts at 160° – 162° , apparently undergoing decomposition. A solution of the freshly-prepared ammonium salt gives a white flocculent precipitate with silver nitrate, followed after a time by a precipitate of silver chloride; and a bulky white precipitate with neutral lead acetate, soluble in excess of the acetate. Barium and calcium chlorides give no precipitate at first, but after standing for some days a precipitate is formed consisting partly of carbonate and partly (in the case of barium) of oxycitra-

conate. In presence of bases hydrochloroxycitraconic acid is mostly decomposed, with complete elimination of chlorine: boiling a neutral solution suffices to render the whole of the chlorine precipitable by silver nitrate. This decomposition takes place in two ways, according as the base is present in excess or in sufficient quantity only to neutralise the acid. Hydrochloroxycitraconic acid neutralised with baryta-water yields a perfectly clear solution, which on boiling gradually becomes turbid, and at length deposits barium carbonate, at the same time evolving carbon dioxide and a disagreeably smelling substance. After filtration the liquid contains only barium chloride and oxycitraconate. But in presence of excess of baryta-water, the liquid remains clear on boiling, and the only products of the decomposition are barium chloride and oxycitraconate. The latter decomposition takes place in a few hours, even at the ordinary temperature.

Hydrochloroxycitraconic acid is readily converted into citramalic acid by the action of sodium-amalgam. When submitted to dry distillation it yields propionic acid, hydrochloric acid, and oxides of carbon:



This decomposition differs entirely from that which monochlorocitramalic acid undergoes when distilled, the product in the latter case, according to Gottlieb, being monochlorocitraconic acid, the carbon nucleus, therefore, remaining unaltered (Morawsky, *loc. cit.*)

Citrartaric Acid, $\text{C}^2\text{H}^2\text{O}^4$. This acid, homologous with tartaric acid, is formed, together with carbon dioxide, hydrochloric acid, and acetone, by heating chlorocitramalic acid with water in a sealed tube; also, together with oxycitraconic acid, when chlorocitramalic acid, its barium salt, or its ethylic ether is boiled with excess of baryta-water (p. 515); and thirdly, by boiling alkaline citramalates with water. On evaporating its aqueous solution, the acid remains as a syrupy deliquescent mass, which slowly crystallises on exposure to the air.

Citrartaric acid is bibasic, its salts have the composition $\text{C}^2\text{H}^2\text{O}^4\text{M}^2$. The barium salt, $\text{C}^2\text{H}^2\text{O}^4\text{Ba}$, separates on supersaturating the acid with baryta-water, as a granular precipitate, easily soluble in hot water, insoluble in alcohol. The neutral lead salt, $\text{C}^2\text{H}^2\text{O}^4\text{Pb}$, is obtained by precipitation, and separates in flocks which become granular on boiling. Basic lead acetate throws down the basic lead salt, $\text{C}^2\text{H}^2\text{O}^4\text{Pb} \cdot \text{PbO}$. The silver salt, $\text{C}^2\text{H}^2\text{O}^4\text{Ag}^2$, is obtained from cold solutions as a white bulky precipitate, which dissolves in boiling water and crystallises on cooling.

Itaconic Acid, $\text{H}^2\text{C}=\text{C} \begin{smallmatrix} \text{CO}^2\text{H} \\ | \\ \text{CH}^2-\text{CO}^2\text{H} \end{smallmatrix}$. The following method of preparing this acid is recommended by Meilly (*Liebigs Annalen*, clxxi. 163). Coarsely pounded citric acid (120–130 grams) is distilled from shallow retorts filled with it up to the neck, as quickly as the frothing of the mass will allow; the oily distillate separated from the water as completely as possible (otherwise it is apt to yield citraconic instead of itaconic acid), is left to crystallise, which it usually does in the course of a night; and the crystals are drained by means of an aspirator, then pressed and recrystallised. The oily filtrate, after heating for four hours in a sealed tube to 150° , yields an additional quantity of itaconic acid. The entire product amounts to about 15 per cent. of the citric acid used.

Reactions with Hydrocyanic Acid.—When equal parts of itaconic acid and anhydrous hydrocyanic acid were heated together to 140° – 150° , a brown liquid was obtained, which when exposed to the air till the free hydrocyanic acid had evaporated, and then distilled, yielded between 200° and 220° , a dark red oil which gradually solidified to crystals of citraconic acid (m. p. 88° – 89°). The syrup heated with sulphuric acid in sealed tubes to 120° , yielded itaconic acid (m. p. 160° – 161°); and the same syrup, after being boiled with strong potash-ley as long as ammonia continued to escape (which lasted nearly a week), then acidulated, and extracted with ether, yielded mesaconic acid (m. p. 202°). The syrupy mass was probably an addition-product of itaconic and hydrocyanic acids, inasmuch as, when treated with soda-ley, it quickly gave off ammonia, even at ordinary temperatures (Harbaglia, *Deut. Chem. Ges. Ber.* vii. 465).

Ethyl itaconate, $\text{C}^2\text{H}^4\text{O}^4(\text{C}^2\text{H}^5)^2$, is obtained by decomposing silver itaconate with ethyl iodide. It is a liquid boiling without decomposition at 230° , and changing after a few days into a viscid polymeric modification, which, however, is reconverted by distillation into the original ether, and like the latter yields itaconic acid by saponification.

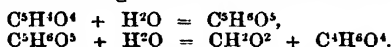
The ether (b. p. 225° – 230°) hitherto regarded as itaconic ether, obtained by passing hydrogen chloride into an alcoholic solution of itaconic acid, appears, from its products

of saponification, to consist mainly of mesaconic ether with a small quantity of itaconic ether (Th. Swarts, *Bull. Acad. royal. Belgique* [2], xxxvi, No. 7 [1873]).

Bromitaconic acid, $C^3H^3BrO^4$, is produced by the dry distillation of itadibromopyrotartaric acid, $C^3H^2Br^2O^4$, the retort being heated from above on account of the slight volatility of the product; and exhausted by means of a Bunsen's aspirator, to prevent the strong frothing which would otherwise take place. The bromitaconic acid distils over partly free, partly in aqueous solution, and may be purified by once recrystallising it from warm (not boiling) water, from which it separates in semi-opaque nodules, or by slow evaporation in crystals resembling those of itaconic acid. The same bromitaconic acid is obtained by heating aconic acid, $C^3H^4O^4$, with hydrobromic acid. It melts with decomposition at 164° , which is the melting point of aconic acid; * dissolves very sparingly in cold water; is resolved by boiling water, or by alkaline carbonates into hydrobromic and aconic acids; and is converted into itaconic acid by the action of tin or zinc on its aqueous solution (Swarts, *Bull. Acad. royal. Belgique*, [2], xxxiii, No. 1, [1872]).

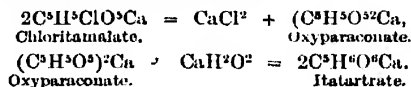
Chloritaconic acid, $C^3H^3ClO^4$, obtained by heating aconic acid with hydrochloric acid, forms crystalline crusts, slightly soluble in cold water, reconverted into aconic acid by boiling water (Swarts).

Oxyitaconic acid, $C^3H^3O^5 = CH(OH) = C \begin{smallmatrix} CO^2H \\ CH^2 - CO^2H \end{smallmatrix}$, is formed as an intermediate product in the decomposition of aconic acid by boiling with baryta-water, the ultimate products of the reaction being formic and succinic acids:



It is a bibasic acid, forming the salts $C^3H^3Ag^2O^5$ and $C^3H^3BaO^5$ (Meilley, *Liebig's Annalen*, clxxi, 153).

Itamalic and Itatartaric Acids (Morawsky, *J. pr. Chem.* [2], x, 68). A solution of chloritamalic acid, (2nd Suppl. 709) exactly neutralised with calcium carbonate, and heated for some time to the boiling point, deposits calcium itatartarate (1st Suppl. 762), which may be freed by washing with boiling water from a second sparingly soluble calcium salt. This latter, which separates from the concentrated mother-liquor in rhombohedral crystals, is the calcium salt of monobasic oxyparaconic acid, $C^3H^3O^5$. When its solution—which is neutral to test-paper—is boiled for some time with a quantity of lime-water containing as much calcium as the salt itself, the liquid again acquires a neutral reaction, and then contains the calcium salt of bibasic itatartaric acid. These changes explain the formation of calcium itatartarate in the manner above mentioned, thus:



Calcium itatartarate, $C^3H^3O^5Ca + \frac{1}{2}H^2O$, gives off its water at 180° , and then exhibits the characters of Roudy's homotartarate (q. v.). The lead salt of itatartaric acid crystallises in tablets having the composition $C^3H^3O^5Pb + H^2O$. [The anhydrous lead salt analysed by Wilm (1st Suppl. 762) appears to have been dried at 100° .]

Oxyparaconic acid, $C^3H^3O^5$, is obtained from its ethereal solution only as a viscid syrup, differing in this respect from oxycitraconic acid. The calcium salt, $(C^3H^3O^5)^2Ca + 2H^2O$, forms, as already mentioned, rhombohedral crystals, which give off their water at 180° (the similarly constituted oxycitraconate forms an uncrystallisable syrup).

Mesaconic Acid. On the constitution of this acid, see p. 513. It separates, after long standing, from a solution of citradichloropyrotartaric acid (p. 514). It was also produced in an attempt to obtain an acid, $C^3H^3O^4$, by treating an alcoholic solution of itamono-chloropyrotartaric acid (1st Suppl. 980) with potassium cyanide, decanting the liquid from potassium chloride thereby formed, and boiling it with potash (Swarts, *loc. cit.*)

On the formation of mesaconic acid from citraconic and itaconic acids, see p. 511 of this volume; also 2nd Suppl. 709. According to Morawsky, the best mode of preparing it is that given by Gottlieb, namely, to boil a weak solution of citraconic acid with nitric acid (iii. 928).

Mesaconic acid melts at 202° (Swarts, Morawsky).

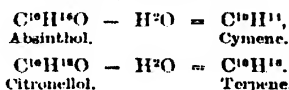
When chlorine is passed to saturation into water in which mesaconic acid is sus-

pended, a solution is formed, which when evaporated gives off sal-ammoniac, and leaves monochlorocitramalic acid.

CITRONELLOL. This is the principal constituent of oil of citronella (*Andropogon Schananthus* or *A. Nardus*), a grass cultivated in Ceylon. According to Gladstone (*Chem. Soc. J.* 1872, 47) it has the composition $C^{10}H^{18}O$, and is isomeric with common camphor and with absinthol; but according to Wright (*ibid.* xii. 318), the chief constituent of the oil (b. p. 210° – 225°) has the composition $C^{10}H^{16}O$; hence it seems probable that the composition of citronella oil (and perhaps of other essential oils) is not quite constant, but varies with the season, the age of the plant, &c.

Citronellol (b. p. 210° – 220°), heated with zinc chloride, yields a large quantity of resin containing 85.4 per cent. carbon, 11.7 hydrogen, and therefore formed by partial removal of the elements of water; also a distillate of water and a hydrocarbon, or mixture of hydrocarbons, containing more hydrogen than cymene.

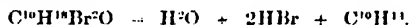
The same citronellol distilled with phosphorus pentasulphide, yielded a hydrocarbon or mixture of hydrocarbons boiling between 160° and 180° , another boiling near 250° , and resinous substances of high boiling point. The portions of the distillate boiling between 220° and 240° yielded, on distillation over sodium, a liquid distilling near 250° , and other liquids of higher boiling point, probably polymeric terpenes, $n^{20}_{D} C^{10}H^{16}$. The action of phosphorus pentasulphide on citronellol is therefore to some extent analogous to that which it exerts on absinthol (p. 1), the action in each case consisting in the formation of a hydrocarbon by removal of the elements of water—



When citronellol is cautiously dropped on cooled phosphorus pentachloride, oxychloride of phosphorus is formed, together with a chlorinated organic substance, which partly breaks up when heated, evolving hydrochloric acid and leaving a mixture of a terpene and a resinous polymeride thereof:



Citronellol unites with bromine, forming a dibromide which splits up into water, hydrogen bromide and cymene:



CITRULLUS. The bitter apple, bitter cucumber, bitter gourd, or colocynth (*Citrullus Colocynthis*, Schrader), is a creeping cucurbitaceous plant which grows abundantly in the Sahara, in Arabia, and on the Coromandel Coast, and is found in some of the islands of the Aegean Sea. The fruit, which is about as large as an orange, contains an extremely bitter and drastic pulp, from which colocynth is obtained. This pulp is said to be eaten by buffaloes and ostriches, but is quite unfit for human food. The seed-kernels, however, which contain but a very small quantity of the bitter principle, are used as food by some of the natives of the African desert. For this purpose the seeds are first freed from pulp by roasting and boiling, and subsequent treading in sacks, and then deprived of their coatings—which are also decidedly bitter—by grinding and winnowing. A single kernel thus separated, has only a mild oily taste, but several, if tasted together, exhibit a distinct bitterness. The average weight of a seed is about 45 milligrams, of which the kernel constitutes only one-half. The kernels contain about 48 per cent. of a fatty oil, and 18 per cent. of albuminous substances, besides a small quantity of sugar, and may, therefore, be regarded as a sufficiently nutritive esculent. The inorganic constituents of the seeds amount to 2.48–2.7 per cent.; the pulp of the fruit contains a much larger proportion, viz., 11 per cent. (Flückiger, *N. Rep. Pharm.* xxi. 46).

CLANDESTINA. The flowers of *Clandestina rectiflora*, a plant growing on the lower Pyrenees, yield to ether two crystalline substances, one of which is yellow, and resembles cholesterolin; the other, called clandestinin, white, soluble in alcohol and ether, insoluble in water and in dilute acids (Hartson, *Chem. Centr.* 1872, 524).

CLARITE (F. Roemer, *Jahrbuch. für Mineralogie*, 1875, 379). This mineral is a dimorphous modification of enargite, found in a bed of heavy spar in the Clara mine near Schapbach, in the Baden Black Forest. It is monoclinic (enargite is rhombic), exhibiting the combination $\infty P. \infty P^{\infty} . 0P . mP$, with perfect cleavage parallel to the clinopinacoid, less distinct parallel to the orthopinacoid. Colour dark lead-grey. Streak pure black. Hardness = 3.5. Sp. gr. = 4.46. Heated in a test-tube, it de-

crepitates violently, and yields a reddish-yellow sublimate of arsenious sulphide and antimonious sulphide, and another of sulphur. In an open tube, a little antimonious oxide is deposited close to the heated mineral, and crystallised arsenious oxide further on. Before the blow-pipe on charcoal it melts very easily, giving off the same vapours, and a very slight deposit of zinc oxide, and leaving, after prolonged reduction, grains of copper in a magnetic slag. Nitric acid dissolves it easily, forming a green liquid, with separation of a white powder. Hydrochloric acid does not decompose it completely, even after long boiling.

The following tables show the composition of the mineral, as determined by analysis, together with that of enargite, and the values calculated according to the formula, $\text{Cu}^2(\text{AsS}_4)^2$ or $3\text{Cu}^2\text{S}.\text{As}_2\text{S}_3$.*

	Cu.	Fe.	Zn.	Sb.	As.	S.	Ag.	
Clarite	46.29	0.83	trace	1.09	17.74	32.92	—	= 98.87
Enargite	47.205	0.565	0.228	1.613	17.599	32.222	0.017	= 99.419
$\text{Cu}^2\text{As}_2\text{S}^6$	48.42	—	—	—	19.07	32.51	—	= 100

The differences between clarite and enargite are shown by the following comparative statement:—

	Clarite.	Enargite.
Crystalline system	Monoclinic.	Rhombic.
Cleavage	Parallel to $\infty R\infty$, and $\infty P\infty$ at 90° .	Very perfect, parallel to ∞P at $97^\circ 53'$, and to $\infty P\infty$.
Hardness	3.5.	3.0.
Sp. gr.	4.46	4.36–4.47.
Colour	Dark lead-grey.	Iron-black.
Streak	Black.	Black.

Clarite is not unfrequently transformed into copper pyrites and indigo-copper, which is not the case with enargite. In the first of these changes, which takes place without alteration of form, and therefore very slowly, the whole of the As_2S_3 is replaced by FeS_2 , which is less soluble in barium sulphide than the arsenic sulphide. The formation of this pseudomorph can take place only out of contact with the air.

Indigo-copper, CuS , may be formed from clarite in two ways, first directly, and secondly after previous conversion into copper-pyrites. In the former case, nothing is seen but particles of fresh lead-grey clarite; in the latter, brass-yellow particles of copper-pyrites imbedded in a black-blue earthy mass. In both cases the formation of indigo-copper appears to be brought about by the oxidation of the iron sulphide (and zinc sulphide), while iron and zinc are dissolved out as sulphates, and arsenic as arsenic acid.

CLAY. A red clay from Hunstanton in Norfolk has been analysed by A. H. Church (*Chem. News*, xxxi. 199). This clay can be isolated by pulverising the limestone in which it occurs, and treating it with dilute hydrochloric acid. The finely divided clay can then be separated from the coarser lumps by levigation. Its composition is as follows:

	Air-dry.	Dried at 100° .	After ignition.
Water	14.73	7.54	—
Silica	52.87	57.33	62.01
Ferric oxide	12.81	13.89	15.02
Alumina	15.65	16.97	18.36
Magnesia	2.65	2.87	3.11
Lime	1.33	1.45	1.56
	100.04	100.05	100.06

Church is of opinion that this red clay is nearly related to that which was dredged up in the 'Challenger' expedition from the greatest depths of the Atlantic Ocean. He regards these red clays as oxidation-products of glauconite.

P. Thénard (*Compt. rend.* lxxxj. 262) describes a clay which was met with during some excavations at Perrigny-sur-l'Ognon, Côte-d'or. It had a deep grey colour when freshly dug, but became black on drying, while at the same time a blue substance was developed like ultramarine in colour. This blue substance becomes olive-green when heated to 120° , and changes to yellow when treated with potash at ordinary temperatures. Neither ammonia nor acetic acid has any effect upon it, and chlorine-water alters it but slowly; very dilute hydrochloric acid however dissolves it imme-

* Dufrenoyite is, perhaps, a third modification.

diately, and destroys its colour, which is not restored by ammonia. This blue substance consists chiefly of ferrous oxide mixed with alumina, and a nitrogenised organic acid in considerable proportion; it does not contain lime or ferric oxide.

A clay from Kum in Persia used for making the well-known water-coolers (alcavrazas), has been analysed by C. v. Hauer (*Verhandl. geol. Reichsanst.*, 1876, 113) with the following results:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaCO ₃ .	MgCO ₃ .	H ₂ O.
43.31	15.14	5.00	26.13	0.27	9.82 = 40.67

with traces of alkali. The porosity which this clay acquires by baking is due to the evolution of carbonic acid from the finely divided calcium carbonate disseminated through it.

C. Bischof (*Dingl. pol. J.* cexi. 128) has analysed a yellow and a red brick-clay from Mogeldorf in Bavaria, with the following results:

	SiO ₂ .	Al ₂ O ₃ .	MgO.	CaO.	Fe ₂ O ₃ .	Loss on heating.
Yellow clay	82.04	9.95	0.64	0.75	3.06	3.67 = 100.11
Red clay	65.93	12.52	2.74	3.36	4.57	11.13 = 100.25

These analyses lead to the following formulæ:



The yellow clay, when washed with water through a sieve having meshes 1.5 mm. wide, left 12.49 per cent. of heavy matter (pebbles, &c.), and the red clay, 10.88 per cent. The former gives a tolerably infusible brick which has not the usual red colour and is not durable; the red clay a fusible brick of good colour. A mixture of the two with a little sand yields a better product. An increase of silica appears to raise the point of fusion. The pyrometric value may be found by multiplying the quantity of silica in the formula by the amount of alumina if the latter figure be less than 1, and dividing if it be greater (*2nd Suppl.* 354). The yellow clay gives the number 6.60, and the red clay 3.98, the higher number showing the higher melting point.

Two very refractory clays from the Moräntsch valley in Carniola have been analysed by A. Paterni (*Dingl. pol. J.* ccvii. 219). They were levigated, and the finest particles dried and analysed with the following results:

Matter insoluble in hydrochloric acid	91.00	91.50
Ferric hydrate	1.50	2.91
Aluminic hydrate	2.75	5.25
Calcium carbonate	trace	trace
Water	1.75	0.34
	100.00	100.00

C. Bischof (*Dingl. pol. J.* ccvii. 51) has also examined the behaviour of fire-clays to glass at high temperatures. Powdered clay was mixed with 2, 4, 6, &c., parts of glass-powder, and the mixtures made up into small prisms were exposed to the heat of melting platinum. The observations consisted in determining the proportions of glass required to induce incipient fusion in the mixture at the given temperature, this condition being indicated by the rounding of the edges, a bright lustre on the surfaces, and a porous vesicular texture in the interior. These appearances were observed in:

Glass-pot clay from Grünstadt after addition of 16 per cent. glass.	
Mühlheim clay	14
Hessian clay	2
Clay from Niederpleis	0
Best Belgian glass pot clay	18
Klingberg clay (I)	18
Klingberg clay (II)	14
Löthay glass-pot clay	14-16
Stourbridge clay	10

From these observations it follows that in general the most refractory clays likewise offer the greatest resistance to the action of glass. In clays nearly related to one another pyrometrically, as those from Grünstadt and from Mühlheim (*2nd Suppl.* 355), the fire-resisting power affords no measure for the relative power of withstand-

* The ferric oxide is included in the general formula, RO.

ing the action of glass. The difference between the best and the moderately good glass-pot clays is much less conspicuous than that between the good and the inferior sorts.

Similar results have been obtained by Bischof (*Bingl. pol. J.* cxviii. 445) with respect to the action of iron-slag on clay. With a slag from Braubach containing in 100 parts:

SiO ₂	Al ₂ O ₃	FeO	MnO	CaO	MgO	P ₂ O ₅	S
33.97	10.60	3.84	9.18	38.93	2.10	0.16	0.78

the above-mentioned indications of fusion were observed with the following proportions:

Hessian clay, after addition of 1 per cent. slag	
Mühlheim clay „	5 „ „
Gründstadt clay „	5-6 „ „
Saarau clay (II) „	6 „ „
Belgian clay „	6-7 „ „
Garnkirk clay „	8 „ „
Saarau clay (I) „	13 „ „
Levigated clay from Zettlitz	14 „ „

Similar results, at least with some clays, were obtained with slags from a Bessemer work at Hörde. In general clays exhibit a parallel variation in their power of resistance to glass and to slags, and are on the whole more easily attacked by slags than by glass.

Suspension of Clay in Water.—From experiments by W. Durham (*Chem. News*, xxx. 57) it appears that the power of water to hold clay in suspension is diminished by addition of acids and of various salts, and increased by addition of small quantities of alkalis, alkaline carbonates, or calcium carbonate. Sterry Hunt (*ibid.* 97) found in like manner that the water of the Mississippi, which contains from 1 to 2 parts of suspended matter, chiefly clay, in a thousand, is clarified in twelve to eighteen hours by addition of sea-water or of sodium chloride, magnesium sulphate, alum, or sulphuric acid: hence the deposits of mud formed at the entrance of the river into the Gulf of Mexico.

M. Schloosing (*Compt. rend.* lxxx. 376, 473) separates the various silicates of alumina which constitute clays, by levigating the clay, and allowing it to deposit in distilled water rendered slightly alkaline, contained in long tubes closed at the bottom, in such a way as to allow the successive layers to be drawn off separately by means of an india-rubber connector. Each layer may be treated in the same manner, so that by successive fractionations the portions may be obtained pure. Clays, such as some kaolins, formed of only one silicate, deposit only one layer.

The silicate, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, has, by this process, been recognised to form the greater portion of kaolin clays, some being composed entirely of it, while others contain two or three silicates, one of which is colloid. Different kaolins differ greatly in the degree of opalescence which they exhibit when agitated in an alkaline liquid, but this property in no way depends upon the chemical composition.

On the determination of clay in arable soils, see Schloosing (*Compt. rend.* lxxviii. 1276; *Chem. Soc. Jour.* 1874, 1010).

Plasticity and Shrinking of Clays (Bischof, *Dingl. pol. J.* cxv. 136).—The plasticity of clay, or its power of yielding with water a mass that may be moulded, is of great importance in a practical point of view, and interesting as a subject of scientific enquiry. Aluminium hydrate, like silicic acid, is capable of assuming the gelatinous form, in which, owing to the peculiar arrangement of the particles, these compounds are able to take up a very large quantity of water, swelling out in an extraordinary degree, and thus enveloping or binding together sandy or earthy matters in a fine state of division. On removing the water by drying, the originally plastic mass shrivels up. This is termed 'shrinking.' Either on drying in the air, or on burning, the particles of clay approach one another more closely, the accompanying admixed constituents also being at the same time drawn together. An increase of density and diminution of bulk thus occur. The capacity for absorbing water in different clays varies as greatly as their plasticity, which increases with their power or tendency to crumble (possibly with the formation of aluminium hydrate). Meagre clays readily absorb water and attain the desired degree of plasticity; 'fat' clays on the contrary become very friable. The former become softer by working, the fat clays stiffer. Many fat clays exhibit the phenomenon known technically as 'water-stiffness' (Wasserstoife), i.e., when softened with a certain quantity of water they have no inclination readily to absorb more. Shortness, or meagreness, depends more upon the presence of undisintegrated mineral particles than on that of sand; a clay rich in sand may, however, be fat, but one rich in unreduced mineral matter never can.

With respect to the condition and law of shrinking, Aron (*Notizblatt des deutschen Zieglervereins*, Jahrgang ix. 167, 339) gives the following facts:—By gradual drying at a temperature increasing to 30° , the weighed portion of clay being placed on a glass plate and two parallel marks cut upon it, and the distance between the marks repeatedly measured, it was found that the shrinking did not continue till the clay was quite dry, but ceased before this point was attained. To a certain point, the shrinking exactly expresses the loss of water; at this point it suddenly stops, just as the clay particles come into contact. Aron terms this point the 'limit of shrinking,' and distinguishes the water dissipated previous to this point as 'water of shrinking' from that subsequently driven off as 'water of porosity.' The sum of the two is total water.

The cubical amounts of shrinking of a pasty mass of clay were found to be equal to the volumes of the water evaporated. The proportion of pores in the dry clay is constant, i.e., independent of the water originally contained. From the fact that the proportion of pores in several chemically different clays is nearly equal, it may be inferred that the smallest particles of clay have a regular spherical shape. This view is confirmed by microscopic observations.

In a plastic mass of clay there is thus a vast number of these little spheres at equal distances suspended in water. The distance between these particles is so small that the attraction between them is considerable, and so a system of capillary tubes is formed in which the expulsion of water by pressure is so opposed that neither the power of attraction of the spherical particles for one another, nor their vertical downward pressure, will permit the water to penetrate through the tubes. Plasticity commences with increase of the distance between the clay particles, and ceases when that increase has attained a certain amount. In shrinking, as water evaporates on the surface, a fresh supply is drawn up from the interior of the mass through the fine capillary tubes mentioned above, the particles approximating throughout the whole mass in obedience to their power of attraction; and this process continues until the particles come into contact, and then room for water is afforded only in the spaces between the particles (water of porosity). In meagre clays these fine spherical particles envelope the irregular-shaped particles of foreign matter. On trying the effect of additions of very fine sand to some washed clay, it was found that, to a certain point, the shrinking power of the clay increases with its progressive meagreness (the water being constant) and the porosity decreases. This point is termed the 'point of greatest density' of the mass.

From the point of greatest density, further impoverishing diminishes the shrinking for an equal amount of water in the pores, but increases the porosity.

COAL. *Composition, Classification, and Heating Power of Coal.*—An elaborate paper on this subject has been published by L. Gruner (*Ann. Min.* 1873, iv. 169; *Dingl. pol. J.* cxviii. 70, 242, 430; *abstr. Jahresh.* 1874, 1187; *Chem. Soc. Jour.* 1875, 295). The value of a coal cannot be accurately determined by its elementary analysis, inasmuch as the heating power depends, not only on the amounts of carbon and hydrogen contained in the coal, but likewise on the manner in which these elements are combined. A more correct estimate of the heating power of a coal is obtained by determining the average amount of coke which it yields. The higher the yield of coke, the greater is the heating power, but this power does not diminish in the same ratio as the yield of coke; thus for a decrease in the yield of coke from 80.4 to 69.0, the heating power diminishes only from 9622 to 8215.

The density of coal varies from 1.25 to 1.35. Those coals which are richest in carbon have the greatest density. The weight of one cubic meter is 700 to 900 kilograms.

The different kinds of coal may be arbitrarily divided into five classes, though there is no distinctly marked division between any two. The classification proposed by Gruner is the following:—

Classification of Coals (Gruner).

Distinguishing property	Elementary composition			Relation of O H	Residue of coke on distillation	Appearance of coke
	C	H	O*			
Dry coal, burning with a long flame	75 to 80	5.5 to 4.5	19.5 to 15	4 to 3	0.50-0.60	{ Powdery, or slightly caked.
Bituminous coal with long flame, or gas coal	80 to 85	4.5 to .5	15 to 10			
True bituminous coal, or smithy coal	84 to 89	5 to 5.5	11 to 5.5	2 to 1	0.60-0.74	{ Fused, but deeply seamed.
Bituminous coal with short flame, or coke coal	88 to 91	5.5 to 4.5	6.5 to 5.5			
Anthracite coal	90 to 93	4.5 to 4	5.5 to 3	1	0.74-0.82	{ Fused, compact, very slightly seamed.
				1	0.82-0.90	Powdery.

The length of the flame depends on the amount of volatile matter; the combustibility of the coal on the nature of the ash. If the ash contains iron and lime, a slag forms; if it contains alumina and silica, it remains in a powdery form, which is more favourable to the combustion of the coal.

The first class, *dry coal with long flame*, is used for making coke. The coke preserves the form of the coal. The sp. gr. of this class of coal is about 1.25; 1 cubic meter weighs 700 kilograms. It is termed *splint coal*. The colour is usually brownish. The elementary composition is given in the table; a proximate analysis gives the following results:—

Coke.	Ammoniacal liquor.	Tar.	Gas.
50—60	12—6	18—15	20—30 per cent.

Volatile matter 50-40 per cent.

The calorific power is on the average 8200-8300 heat-units. This coal is found in Derbyshire, Staffordshire, and Lanarkshire. As soon as the carbon exceeds 80 per cent., and the oxygen is under 15 per cent., this class of coal begins to cake on heating.

The Belgian coal called *fusain minéral* contains an amount of carbon which would include it in this class; but its coke is always powdery. It has a lower calorific power.

2. *Bituminous Coal with Long Flame* (gas coal).—The coke obtained from this coal is always caked together. The coal itself is hard, the fracture laminated. The sp. gr. is 1.28-1.30; the weight of 1 cubic meter 700-750 kilograms. The colour is pure black with a strong lustre. The proximate composition is—

Coke.	Ammoniacal liquor.	Tar.	Gas.
60—68	5—3	15—12	20—17 per cent*

Volatile matter 40-32.

Yield of gas from 1 kilogram 240—260 litres.

Calorific power 8500—8800 heat-units.

This coal is found in the coal measures of the *Pas-de-Calais*, and of the Loire in France, at Mons in Belgium, and at Newcastle.

3. *True Bituminous or 'Smithy Coal.'*—Coals belonging to this class have a pure black colour and high lustre; they are brittle with laminated fracture. They fuse when burning, leaving the coke in a compact cake. They are, therefore, peculiarly adapted for a smithy. Sp. gr. 1.3. Weight of a cubic meter, 750-800 kilograms.

Proximate analysis:—

Coke.	Ammoniacal liquor.	Tar.	Gas.
68—74	3—1	13—10	16—15

Volatile matter, 32-26.

Calorific power, 8800-9300 units of heat.

Found in the coal measures of *Pas-de-Calais* in France; in the neighbourhood of

* The oxygen includes nitrogen; but the latter seldom exceeds 1 per cent. of the combustible material.

Liège and Mons in Belgium; in Westphalia; in Yorkshire; and near Newport in Wales.

4. *Bituminous Coal with Short Flame, or 'Caking Coal.'*—Coal belonging to this class exhibits the same properties as that belonging to the one immediately preceding; its lustre is, however, not so great. It is very brittle, and although it is termed 'dure' in France, this means that it does not burn away quickly. It does not contain much volatile matter, and is consequently difficult to kindle.

Proximate analysis gives the following results:—

Coke.	Ammoniacal liquor.	Tar.	Gas.
74—82	1—1	10—12	5—12 per cent.

Volatile matter, 26—18. Calorific power, 9300—9600 units of heat. Sp. gr. 1·3—1·35. Weight of a cubic meter, 800 kilograms.

Sources in France—Creuzot; near St. Etienne in the basin of the Gard; in the coal measures of Brissac, Abrun, &c.; in Belgium, near Charleroy; and in Wales, near Cardiff.

One kilogram of this coal evaporates 9·75 kilograms of water.

5. *Anthracite Coal.*—This coal forms the link to pure anthracite. It is black, and shows dull streaks. Its cohesion is slight, but increases the nearer it approaches the character of anthracite.

Coke.	Ammoniacal liquor.	Tar.	Gas.
82—90	1—0	5—2	12—8 per cent.

Volatile matter, 18—10. Calorific power, 9200—9500. Sp. gr. 1·35—1·40. Weight of a cubic meter, 850 kilograms. It is adapted for use in the blast furnace. It is met with in the neighbourhood of Valenciennes and in the coal measures of the Sarthe, of the Roannais, and of the Lower Loire, the Gard, the Creuse, &c.; also in Charleroy, Swansea, and Merthyr Tydvil. It occurs also in Pennsylvania.

One kilogram calculated without ash evaporates 9·15 kilograms of water, but containing, as it usually does, 10—11 per cent. ash, 8·12 kilograms.

C. Hilt (*Dingl. pol. J.* cccviii. 424) likewise regards the yield of coke, together with the amount of ash, as of especial importance in the valuation of coal. He gives a classification of coals according to the ratio between the quantities of bitumen and coke which they yield when ignited in a covered crucible.

	men	Coke	Bitumen	Coke
1. Anthracitic coal	1	20	1	9
2. Flint-coal (old) yielding but little gas	1	9	1	5·5
3. Caking coal	1	5·5	1	2·0
4. Caking gas-coal	1	2	1	1·5
5. Flint-coal (young) yielding much gas	1	1·5	1	1·25
6. Gas coal	1	1·25	1	1·1

If the amount of bitumen or volatile matter be expressed in percentage of that of the coke free from ash, these coals may be characterised as follows:—

Bitumen.				Bitumen.			
No. 1 contain	5	to 10	per cent.	No. 4 contains	33·3	to 40	per cent.
2	10	15·5	"	5	40	44·4	"
3	15·5	33·3	"	6	44·4	48	"

No. 1 includes the varieties of ordinary anthracite.

No. 2 includes such coals as the 'smokeless seam coal' of Cardiff.

No. 3 includes the varieties of coal used for general manufacturing purposes.

No. 4 is a good gas coal, but yields little coke, and this of too porous a nature.

No. 5 and 6 are chiefly used in open stoves; they burn with a bright flame, accompanied by a considerable quantity of smoke.

Analyses of Russian Coals.—Immense deposits of coal are found in the basin of the Donetz; much of it is of exceptional purity, leaving only 2 or 3 per cent. of residue in the grate. The following are the results obtained with three samples of coal and one of lignite from this region:—I. From Groucheski is a greyish-black coal having a very brilliant metallic lustre. It is very hard and compact, and keeps its form while burning. It burns without flame or decrepitation, it contains pyrites.—II. From Mioueki is deep black and very brilliant. It is very friable, and burns without much smoke. It is well adapted for the smithy, and is equal to, and, in some respects, superior to the Welsh coal much used in the English navy, the analysis of which appears in the *Journal of the Chemical Society*, 1872, p. 91.—III. From Galoubowski, is black and brilliant, with a slightly conchoidal fracture. It is compact, and burns with more smoke than II.—IV. A lignite from Riazan, known as Teula lignite. It occurs in slabs which break down, with conchoidal fracture, into laminated

It contains abundance of pyrites, more water for the most part than the sample analysed, and often leaves 30 per cent. of residue on the grate.

	I.		II.		III.		IV.	
	Crude	Pure	Crude	Pure	Crude	Pure	Crude	Pure
Water	4.08	—	1.39	—	4.88	—	9.39	—
Ash	1.57	—	0.23	—	1.42	—	16.86	—
Hydrogen	1.27	1.35	4.43	4.50	4.75	5.07	4.49	6.09
Carbon	91.20	96.66	89.97	91.45	77.47	82.67	54.37	73.72
O, N, S	1.88	1.99	3.98	4.05	11.48	12.26	14.89	20.19
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Per cent. of coke	91.04	80.61	00.88	37.03
Heat of combustion in gram- degrees	8289	8695	8021	7687

(Scheurer-Kestner and Meunier-Dollfus, *Ann. Chim. Phys.* [5], ii. 325; *Compt. rend.* lxxvii. 1385).

The following analyses of Russian coal are by S. Kern (*Chem. News.* xxxi. 133; xxxii. 70).

1. *Government of Novgorod*.—River Priekha. This is properly a lignite. The dried coal yields 62.2 per cent. of coke and 6200 cubic feet of gas per ton.

2. *Dried coke from the Priekha coal*, suitable for reverberatory furnaces.

3. *Government of Toula*.—Obidmovo. Coal found 30 to 70 feet from the surface.

4. *Government Riasane*.—Mouravna Colliery.

5. Coal from Vaschour, Ural Mountains.

6. *Donetz Mountains*.—Grouschevka mine.

7. *Donetz Mountains*.—Village of Alexandrovka. Good coal yielding a compact coke.

8. *Donetz Mountains*.—Village of Ouspenskoe.

Government Toula.—9. Kiertzi village, on the River Oka. 10. Krasni Cholmi village. 11. Vialino village, in the Odoievsky district. 12. Malëvka village, Bogoroditsk district.

Government Kalouga.—13. Zelenino village. 14. Znamensky village, Lihkvin district.

Government Ekaterinoslaw.—15. Near Mr. Illovaiski's village; yields 10,600 cubic feet of gas per ton; and 74.7 per cent. of compact coke.

Government Simbirsk.—16. Near Syrane town, on the Volga.

Caucasus.—17. On the Rivers Oubane and Choumar; yields a compact coke.

18. *Donetz Mountains*, on the River Bolshaia-Nesvitaia. This is a good anthracite.

	Carbon per cent.	Volatile matter per cent.	Ash per cent.	Calorific value	Sulphur per cent.	Hygroscopic water per cent.
1	56.7	46.8	18.5	4500 units	3.6	18.9
2	78.03	10.71	11.26	5910 "	—	—
3	39.14	42.65	18.23	4100 "	3.23	2.55
4	17.60	66.26	8.61	5485 "	2.4	7.53
5	77.86	12.30	2.72	7320 "	—	7.12
6	90.08	7.22	1.98	7640 "	—	—
7	60.92	29.00	1.08	7690 "	0.36	—
8	64.85	28.90	6.25	7970 "	0.87	—
9	22.54	27.78	49.68	3000 "	3.07	—
10	52.00	31.32	16.68	4000 "	—	—
11	39.68	52.46	7.92	4000 "	2.13	—
12	34.88	42.36	22.36	3500 "	32.0	32.0
13	30.35	48.36	21.29	3560 "	—	—
14	35.70	44.24	20.06	4200 "	—	20.05
15	72.22	24.47	2.48	6900 "	—	0.83
16	17.2	37.30	28.40	3500 "	—	17.10
17	58.85	37.99	3.16	7000 "	—	—
18	98.27	4.92	1.31	7600 "	0.27	—

On two Coals from Cape Breton, Nova Scotia, their Cakes and Ashes, see H. How (*Chem. Soc. J.* 1874, 325).

Analyses of Japanese coals have been made by H. S. Munroe (*American Chemist*, v. 120). These coals, which are found in 25 out of the 62 provinces of Japan, are obtained principally from the island of Yesso, on which there occur three coal-fields, viz. in Kayanoma, Horumui, and Sorachi. The last two are situated on the river Ishikari, about 30 miles from one another, and are perhaps connected. The Kayanoma field, on the west coast of Yesso, latitude $43^{\circ} 10'$, consists of at least six seams from 3.5 to 8 feet thick. In the Ishikari field four or five seams have been found, from 3 to 5 feet thick. From the numerous tables accompanying Munroe's paper the following may be selected as giving a good example of the composition of Japanese coal:

	Midzu-nuki	Hon-shiki (fresh)	Hon-shiki (stored)	Tateiri	Furu-shiki	Horumul 1	Horumul 2
Moisture	3.714	5.360	4.095	5.060	1.342	5.194	8.470
Carbon	57.689	65.221	64.412	56.283	69.049	72.982	68.842
Hydrogen	4.620	5.222	4.911	4.124	5.256	5.300	4.771
Oxygen (and N) .	10.144	10.118	9.940	10.271	7.172	13.841	15.180
Sulphur	3.765	1.607	1.449	1.178	2.386	0.363	0.472
Ash	20.068	12.472	16.193	23.084	14.795	2.330	2.256
Hydrogen and Oxygen (combined)	10.062	10.033	9.832	10.205	6.718	14.221	15.727
Free Hydrogen . .	3.502	4.107	3.818	2.990	4.510	3.720	3.024
Heating power . .	5625	6373	6262	5351	6872	6895	6329
Evaporating power .	10.48	11.88	11.67	9.97	12.81	12.85	11.80
Heat of combustion .	2504° C.	2476° C.	2556° C.	2510° C.	2605° C.	2678° C.	2631° C.

	Sorachi	Kadzuno (lignite)	Mitake	Karatzu	Taka-schima	Mean
Moisture	2.928	14.346	4.536	2.690	1.320	4.689
Carbon	77.040	62.149	69.280	69.436	78.633	67.585
Hydrogen	5.685	3.368	5.524	5.156	5.816	4.979
Oxygen (and N) .	11.014	16.395	4.888	11.920	8.721	10.800
Sulphur	0.542	2.116	3.488	1.177	0.659	1.699
Ash	2.791	1.636	16.284	9.621	4.861	10.448
Hydrogen and Oxygen (combined)	11.041	17.094	4.149	12.060	8.401	10.800
Free hydrogen . .	4.458	1.459	5.063	3.816	4.876	3.779
Heating power . .	7492	5286	7072	6664	7747	6499
Evaporating power .	13.96	9.85	13.16	12.42	14.44	12.11
Heat of combustion .	2627° C.	2374° C.	2615° C.	2681° C.	2644° C.	2666° C.

Alteration of Coal by Exposure to the Air.—A series of experiments has been made by E. Richters (*Dingl. pol. J.* cccxv. 315, 449; cccxvi. 317), with the view of determining whether the absorption of oxygen by coal at ordinary temperatures is attended with oxidation of carbon or hydrogen. Coal-powder heated to 180° – 200° takes up oxygen and gives off carbon dioxide and water. The absorption of oxygen is however greater than that which corresponds with the quantity of the gases evolved, and it ceases as soon as the hydrogen and oxygen in the coal stand to one another in the proportion to form water. From these facts Richter deduces the following conclusions:

1. The property of coal to take up oxygen when slightly heated, is essentially determined by its amount of available (combustible) hydrogen, this hydrogen being oxidised, together with a certain portion of the carbon, whereby water is formed, and part of the oxygen enters directly into the composition of the coal.

2. Different portions of the carbon of coal exhibit at about 190° , different affinities for oxygen, the smaller portion (5 or 6 per cent.) uniting with the oxygen to form carbon dioxide, while the remainder exhibits at that temperature but little affinity for oxygen.

These laws likewise hold good for ordinary temperatures. At lower temperatures

the absorption of oxygen is partly physical, the rapidity of the absorption being proportional to the surface attraction of the coal, as exhibited by its hygroscopic action. In the first 24 hours 20 grams of different kinds of coal were found to absorb from 2 to 9 cubic centimeters of oxygen. The absorptive power of coal diminishes with time, but the decrease does not appear to be due to condensation of carbon dioxide on the coal.

At higher temperatures the oxidation processes above described go on more quickly. The moisture of the coal has only an indirect influence in accelerating the oxidation. In presence of water, the pyrites, which is always contained in coal, becomes oxidised, and this oxidation is attended with a rise of temperature by which the oxidising action is accelerated. The ferric oxide resulting from this action also takes up a larger space than the iron sulphide, and by its formation the coal may be more or less disintegrated and rendered more accessible to the air. Lastly the iron may also carry over oxygen to the carbon, the ferric oxide being thereby reduced to ferrous oxide, which again takes up oxygen from the air, then gives it up and so on. The influence of daylight on the oxidation is perceptible only in old coals in which the absorbing power is already considerably reduced; fresh coals oxidise in the dark as quickly as when exposed to light. The spontaneous combustion of coal takes place when the absorption and oxidation processes above described act together under favourable circumstances, and at the same time the heat developed by the oxidation is not conducted away.

The gradual oxidation or 'weathering' of coal on exposure to the air is attended with a decrease of heating and caking power, and a diminished capacity of yielding coke and gas. It takes place most quickly in coals fresh from the pit, and diminishes in intensity as the oxidation advances. The absorption of oxygen at first increases the weight of the coal, but afterwards, when the temperature has been raised by the oxidation to 170° – 190° , a perceptible decrease of weight takes place.

A weathered coal will for the most part yield more or less coke than the same coal when fresh, according as the diminution of its hydrogen exceeds or falls short of the increase of its oxygen.

The quantity and quality of the gas yielded by coal depends essentially on its amount of available (unoxidised) hydrogen. If in consequence of weathering a part of the hydrogen has entered into combination with oxygen, this hydrogen, at the temperature of the gas-retorts, will, partly at least, be lost for the preparation of illuminating gas. The quantity of gas obtained from fresh coal is in fact always greater than that from weathered coal.

Caking power of Coal.—This quality depends mainly on the amount of hydrogen in the coal, and is lost altogether when the coal is heated for some time to 105° , whereby the hydrogen is driven off; in weathered coal which has lost more or less of its hydrogen by oxidation, the caking power is also considerably diminished.

The caking powers of different coals may be compared by determining the relative quantities of finely levigated quartz-powder which may be mixed with them, so that the cake formed by igniting the mixture in a platinum crucible as long as combustible gases are given off, may just bear a given weight without being crushed (Richter, *Dingl. pol. J.* xciv. 71).

H. Fleck (*Dingl. pol. J.* xciv. 430) classifies coals according to the relative quantities of combined hydrogen, and of free hydrogen available for combining with carbon, which they contain. The quantity of hydrogen in coal is for the most part greater than that which is required for combining with the oxygen and nitrogen. Hence if the sum of the quantities of oxygen and nitrogen = S, and that of hydrogen $H = H_1 + H_2$, where H_1 denotes the free and H_2 the combined hydrogen, the value of H_2 will be approximately $\frac{S}{8}$, since 1 part by weight of hydrogen combines with 8 parts of

oxygen [and the amount of nitrogen is small in comparison with that of oxygen]. If then H and S are known, H_1 can easily be found. The physical properties of coal seem to depend mainly on the proportion between the free and combined hydrogen.

In the following table, deduced from the analyses of a large number of coals from Upper Silesia, the quantities of free and combined hydrogen are referred to 1000 pounds of coal.

1000 lbs. of	lbs.	lbs.
Caking coals	Contain more than 40 free, less than 20 combined H.	
Difficultly caking gas-coals	Contain more than 40 free, more than 20 combined H.	
Non-caking gas-coals and sand-coals.	Contain less than 40 free, less than 20 combined H.	
Flint-coals, anthracites	Contain less than 40 free, more than 20 combined H.	

The caking power of a coal increases therefore with the amount of free, and diminishes with the amount of combined hydrogen. A coal may be rich in free hydrogen, and nevertheless may possess but little caking power, namely, when it also contains a large amount of combined hydrogen.

According to F. Muck (*Chemische Aphorismen über Steinkohlen*, Bochum, 1873; *Jahresb. f. Chem.* 1873, 1089), Westphalian caking coals (yielding when heated a coherent, fused, and decidedly tumefied mass) cannot be placed in Fleck's classification. According to the latter, such coals should contain more than 40 lbs. of available, and less than 20 lbs. of combined hydrogen to 1000 lbs. of carbon, whereas Muck, out of 49 samples, finds the amount of available hydrogen to be in 25 samples below 40, in 11 below 36, and in 4 below 30 lbs. to 1000 lbs. of carbon. Fleck is of opinion that the degree of tumefaction of coals in coking likewise increases with the amount of available hydrogen. According to Muck, on the other hand, the greatest tumefaction takes place in those coals which have the smallest total amount of hydrogen, and of combined hydrogen, and yield the largest proportion of coke, whereas the available hydrogen has no influence on the tumefaction. With a nearly equal total amount of hydrogen, the yield of coke decreases with increasing amount of combined hydrogen, and with decreasing amount of free hydrogen. With nearly equal amount of available hydrogen, the yield of coke decreases as the total amount of hydrogen increases. With nearly equal combined hydrogen the yield of coke decreases as the proportion of free hydrogen increases. Coals from the same pit often differing from one another in external appearance (lustre, structure, &c), yield less coke in proportion as they contain a greater proportion of available, less of combined, and more of total hydrogen. Coals of equal percentage composition may contain hydrogen combined in various ways; they are then isomeric with one another, and in spite of their agreement in chemical composition, they yield different quantities of coke. The determination of the yield of coke is regarded by Muck as affording a very good criterion of the character of a coal.

The bituminous shales (*Brandschiefer*) often found accompanying caking coals contain a larger amount of available hydrogen and of volatile constituents in general (calculated on the substance free from ash), than coals from the same field, also regarded as free from ash.

Gases enclosed in coal. An examination of the gases enclosed in coals from the South Wales basin, and of the gases evolved from blowers, and by boring into the coal itself, has been made by J. W. Thomas (*Chem. Soc. J.* 1875, 793).

The method of collecting the gases is as follows:

Slices of coal were sawn out of the middle of large cubes, and a strip about $\frac{1}{2}$ of an inch in thickness and 6 to 8 inches long was next cut from the middle of this slice, the edges being rounded off, so as to make it slide readily into a glass tube of the proper diameter. The coal was brushed with a feather to remove adhering dust, and quickly placed in the glass tube, one end of which had previously been drawn out into a long narrow neck, so as to form a connection with a Sprengel mercurial pump. The other end was then sealed off before the blowpipe, at a sufficient distance from the coal to prevent any material rise in temperature. The usual water-joint connection was then made with the Sprengel pump, the air exhausted as quickly as possible, until almost a perfect vacuum had been obtained, and the last portion of the gases which was brought over collected and subjected to analysis. Many of the bituminous and steam coals of the South Wales coal-field are of a porous nature, and far from hard or dense; and from their physical aspect it appeared probable that, on withdrawing the air from around the strips of coal, and on the formation of a partial vacuum, a large portion of the gases enclosed in the coal would escape. This however was not found to be the case, as very little gas was evolved from any of the coals examined, even when almost a complete vacuum had been obtained, and the amount of gases so given off rarely exceeded 2 or 3 c.c. per 100 grams of coal. Some of the steam and bituminous coals, which were hard and laminated, as well as the still harder and denser anthracites, evolved only traces of gas, whilst the enclosed gases were rapidly given off as soon as the temperature was raised.

When the whole of the air had been removed, the tube containing the coal was immersed in a vessel of boiling water and kept at a temperature of 100° for about seven hours, or until the mercury pump ceased to bring over any appreciable quantity of gas. The gases thus evolved were collected in graduated tubes.

From 10 to 30 grams of coal were usually employed in each experiment, according to the nature of the coal and the quantity of gas evolved, a very small quantity of anthracite being sufficient to furnish an ample amount of gas for analysis, whilst highly bituminous coals gave off so little gas that 20 grams of coals were required to yield the necessary volume.

The rapidity with which the occluded gases are evolved in a vacuum at 100° depends upon the hardness of the coal and the quantity of gas enclosed. By far the portion of the gases given off at that temperature is brought over by the pump in a first three hours.

A complete expulsion of the gases is not however effected at 100°, or even at 200°, a considerable quantity still remaining imprisoned in the pores of the coal after it has been kept at that temperature. In a few instances this was proved by heating the coal to 300°, or close upon the point at which decomposition begins.*

The coals examined were of three kinds, bituminous coal, also called house-coal; steam coal, intermediate in character between bituminous coal and anthracite, and very abundant in the South Wales basin; and lastly anthracite.

The gases from these three classes of coal differ in quality and still more in quantity. The bituminous coals, when on or near the surface, contain little or no marsh-gas, but usually a large proportion of carbon dioxide. The quantity of gas which they yield is much smaller than that given off from steam coal or from anthracite. The bituminous character of a coal might indeed be inferred, without much risk of error, from the quality and quantity of the evolved gases.

The smallness of the quantity of marsh-gas usually enclosed in bituminous coals accounts for the fact that seams of these coals can be and are worked all over South Wales with naked lights. The few samples taken from deeper levels which contained a high percentage of marsh-gas still differ materially from the steam coal and anthracite, by giving off comparatively small quantities of gases. The real difficulty of working these seams arises, in fact, not so much from the presence of marsh-gas as from that of carbon dioxide. None of the coals examined yielded carbon monoxide.

Steam coals evolve a much larger quantity of gases than bituminous coals, and their composition also differs by showing invariably a very high percentage of marsh-gas—as much, in fact, as 87 per cent. The volume of gas depends in a great measure upon the hardness and porosity of the coals, and upon the time which has elapsed since they were removed from their respective seams or veins; this latter remark applies equally to all coals.

Hard compact steam coals, especially those showing laminated structure, evolve a quantity of gas approaching to that given off by anthracites.

Steam coal also gives off a considerable quantity of gas at 200°, after having been previously heated at 100° for some hours.

Anthracites yield by far the largest gas-volumes, e.g., sample 14, in the following table, of specific gravity 1.35, and giving on analysis 2.67 per cent. of hydrogen, yielded from 100 grams of coal as much as 600 c.c. of gas, when heated at 100° for seven hours. On heating it to 200° for eight hours, close upon 1,600 c.c. of gas were obtained, whilst at 300° a still further quantity was given off, the gas obtained amounting altogether to 1876.9 c.c. per 100 grams of coal.

The composition of the gases evolved from anthracites closely resembles that from steam coals. The only difference appears to be that the anthracites from the western part of the coal-basin occlude more marsh-gas and less carbon dioxide (sample 13), and that they are absolutely free from oxygen, while steam coals, as a rule, showed traces of oxygen, probably derived from air diffused into the coal during the time of handling it.

The gases evolved from anthracite at 100°, 200°, and 300, are analogous in composition, in so far as they consist of carbon dioxide, marsh-gas, and nitrogen only; but the percentage of the latter is reduced to a mere trace (in fact, within the analytical limits of error) at the higher temperatures; the percentage of carbon dioxide also decreases, leaving a gas-volume consisting almost entirely of marsh-

The following table shows the quantities of gases evolved, as well as the percentage composition:—

* This shows that Meyer's method of expelling the gases by boiling the coal with de-aerated water (2nd Suppl. 368) could not have yielded the whole of the gases enclosed in the coals. Other sources of inaccuracy in this method are to be found in the well-known difficulty of removing the whole of the gases from water, even under reduced pressure, and in the solubility of carbon dioxide in water.

No. of sample	Gas evolved by 100 grams of coal, at 100° under vac.	Composition of Gases			
		Carbon dioxide	Oxygen	Marsh-gas	Nitrogen
1	55.9 c.c.	36.42	0.80	—	62.78
2	61.2 c.c.	16.77	2.72	0.40	80.11
3	55.1 c.c.	5.44	1.05	63.76	29.75
3a	73.6 c.c.	12.34	0.64	72.51	14.51
4	194.8 c.c.	5.04	0.33	87.30	7.33
5	250.1 c.c.	13.21	0.49	81.64	4.66
6	218.4 c.c.	5.46	0.44	84.22	9.88
7	147.4 c.c.	18.90	1.02	67.47	12.61
8	375.4 c.c.	9.25	0.34	86.92	3.49
9	149.3 c.c.	11.35	0.56	73.47	14.62
10	215.4 c.c.	5.64	0.54	82.70	11.12
11	24.0 c.c.	22.16	6.09	2.68	69.07
12	39.7 c.c.	9.43	2.25	31.98	56.34
13	555.5 c.c.	2.62	—	93.13	4.25
14	600.6 c.c.	14.72	—	84.18	1.10

1. Bituminous, from a level above South Pit, Plymouth Iron Works.
2. Bituminous, from South Pit, Plymouth Iron works.
3. Bituminous, from Cwm-Clydach.
- 3a. Semi-bituminous, from Bute Merthyr Colliery, Rhondda district.
4. Steam, from Bute Merthyr Colliery; 2 ft. 9 in. seam.
5. Steam, from upper 4 ft. seam, Navigation Colliery.
6. Steam, from upper 4 ft. seam, Dunraven Colliery.
7. Steam, from upper 4 ft. seam, Cyfartha.
8. Steam, from 6 ft. seam, Bute Merthyr Colliery.
9. Steam, from 6 ft. seam, Dunraven Colliery.
10. Steam, from 9 ft. seam, Duffryn Colliery.
11. Bituminous, from Bettwys Coal, Ogmere Valley.
12. Bituminous, from Lantwit.
13. Anthracite, from Hoville Court.
14. Anthracite, Watney's Llanelly.

It is necessary to observe that the preceding conclusions as to the large quantities of gas evolved from anthracites, apply only to these coals when examined in the laboratory; and it must not be taken for granted that, because a coal contains a large quantity of occluded gases, even if they consist mainly of marsh-gas, the seam or vein from which it is derived is a fiery one, and requires great caution in working. The very reverse is indeed often the case. Steam coal yields less gas than anthracite, but it is not therefore safer to work. Before removal from the vein it holds enclosed a much larger quantity of gas, but being less hard and more porous than anthracite it allows the gas to escape from it in very much larger quantities. The volume of gas rushing out from the working faces of most deep steam coals is enormous, whereas little is evolved from the working face of anthracite coal. The great hardness and jet-like structure of the latter accounts in a great measure also for the large volume of gas which it holds enclosed, and it is probable that its formation must have taken place under such immense pressure that the gases generated during the metamorphosis of the organic matter into anthracite were not able to make their escape.

Gases evolved from Blowers.—To collect these gases the crack or rent in the rock from which they issued was carefully filled in with clay, to prevent the diffusion of atmospheric air, and a small hole was left in the centre, into which a glass funnel was introduced, and made air-tight with clay. Glass tubes which had previously been drawn out at each end into a small neck were connected with the funnel by means of india-rubber tubing, and screw-clamps were placed upon the india-rubber connections at both ends of the tubes.

When the blower was a strong one, it was only necessary to allow the gas to pass through the tubes for about ten minutes, in order to displace the air. In most cases however it was found impracticable to displace the whole of the air in this manner, as the gas found several outlets through the many cracks in the rock. A double-acting syringe was therefore employed, and when all the air had been displaced, the tubes

were slightly warmed, the clamps screwed tight, and the tubes taken without delay to the lamp station for the purpose of sealing the ends before a blowpipe flame.

To compare the blower gases with the gas evolved by the coal won in the gallery or heading in which the blower-gas was collected, a hole was drilled into the solid face of the coal itself, and the gases collected in the manner above mentioned. The same method was also used for collecting those blowers which in some instances were carried to the surface of the pits.

The following table shows the composition of blowers and gases from borings:—

No. of sample	Whether a blower, or obtained by boring into coal	Composition of the gas				
		Methane or marsh-gas	Ethane	Carbon dioxide	Oxygen	Nitrogen
1	Blower	97·65	—	0·50	—	1·85
2	Boring	97·31	—	0·38	—	2·31
3	Blower	96·74	—	0·47	—	2·79
4	Boring	96·54	—	0·44	—	3·02
5	Boring	74·86	—	0·15	4·69	20·30
6	Boring	97·37	—	0·42	—	2·21
7	Boring	95·42	—	0·60	—	3·98
8	Blower	94·84	—	0·10	—	5·06
9	Blower	95·05	—	4·26	—	0·69
10	Blower	47·37	—	0·90	10·15	41·58
11	Blower	95·47	—	0·62	—	3·91
12	Blower	95·51	—	1·96	—	2·53
13	Blower	94·78	0·90	0·72	—	3·60
14	Blower	95·56	—	0·35	0·11	3·98

1. Gases obtained from the top rock of the 6-ft. seam, Dunraven Colliery, Treherbert, 226 yards from the surface.

2. Gas obtained by boring into the coal, 6-ft. seam, Dunraven Colliery, 25 yards from the surface.

3. Gas from top rock of 4-ft. seam of the same colliery, and at the same depth.

4. From the same seam and at the same depth by boring.

5. From 6-ft. seam of the Fochriew Colliery, No. 2, Merthyr district, 395 yards from the surface, by boring.

6. From the 9-ft. seam of the same colliery, by boring 454 yards from the surface.

7. From the 4-ft. seam of the South Pit, Plymouth Iron Works, Merthyr, by boring 300 yards from the surface.

8. From the top rock of the same seam 300 yards below the surface; water oozed out together with the gas: hence the low percentage of carbon dioxide.

9. Gas from top rock of 6 ft. seam, Forchammon Colliery, Aberdare district, 230 yards from the surface.

10. Gas from a rent in the top rock of the 4-feet seam No. 2 Colliery, Rhondda district.

11. From a heading connecting the upcast and downcast shafts, Bute Merthyr Colliery, Rhondda district, situated about 20 yards above the 2 ft. 9 in. seam, and 80 yards from the surface.

12. Gas obtained on the floor of a hard heading between the 6-ft. and 9-feet seam, Maestog Merthyr Colliery, 140 yards below the surface.

13. Gas obtained from the lamp-room, Llwynypia Colliery, Rhondda District, and brought up to the surface for lighting purposes. Several analyses showed that it contained a small quantity of some hydrocarbon, probably ethane, in addition to methane. Some of the other samples likewise appeared to contain traces of this hydrocarbon.

14. Gas collected from the side of Cwm Park Brook, Ystrad Rhondda district where it escaped in large quantity.

These blower gases from the South Wales coal-field exhibit great similarity of composition amongst themselves; from those of the North of England coal-fields analysed by Playfair (*Records of the Museum of Economic Geology*, June 1846), they differ in their high percentage of marsh-gas and comparatively low percentage of nitrogen.

COAL (CANNEL) AND JET, GASES ENCLOSED IN. 533

Gases enclosed in Cannel Coals and Jet (J. W. Thomas, *Chem. Soc. J.* 1876, ii. 144). The method used for obtaining the enclosed gases was similar to that described above, excepting that Florence flasks, having their necks drawn out and bent over, were substituted for glass tubes when Scotch cannel was employed, a large quantity of coal being required to furnish the necessary volume of gas. These coals were broken in a mortar and passed through a sieve having 9 meshes to the inch, and the dust was removed by a sieve having 64 meshes to the inch.

The following table shows from whence the cannel coals and jet were obtained:—

No. of sample	Description	District
No. 1	Wigan cannel $\frac{1}{2}$ seam, 350 yards deep.	Wigan Arley Mine, Lancashire coal-field.
2	Wigan cannel $\frac{3}{4}$ seam, 600 yards deep.	Lancashire coal-field.
3	Scotch cannel (Heywood cannel, Wilsontown).	Lanark.
4	Scotch cannel (Lewmahago).	
5	Whitehill cannel shale, Lasswade.	Edinburgh.
6	Whitby jet (finest quality for ornaments).	Whitby.

Cannel coals are usually very hard and close-grained, fracturing conchoidal, without crumbling, and when placed in a vacuum do not evolve any appreciable quantity of gas. No. 1 was somewhat porous, and resembled in appearance the hardest steam coals of the South Wales basin.

Composition of Gases.

No. of sample	Gas evolved by 100 grams of coal at 100° under a vacuum	Carbon dioxide	Methane or marsh-gas	Ethane or hydride of ethyl	Butane or diethyl.	Nitrogen
1	421.3 c.c.	6.44	80.69	4.75	—	8.12
2	350.6 c.c.	9.05	77.19	7.80	—	5.96
3	18.6 c.c.	53.94	—	—	—	46.06
4	55.7 c.c.	84.55	—	—	{C ² H ⁶ } 0.91	14.54
5	55.7 c.c.	68.75	—	2.67	—	28.58
6	30.20 c.c.	10.93	—	—	86.90	2.17

The coals examined by Meyer from the Newcastle and Durham coal-fields did not contain any hydrocarbon other than marsh-gas (*2nd Suppl.* 368); and the bituminous anthracite and steam coals above described likewise contained only CO², CH⁴, O and N as occluded gas.

Cannel coals however differ considerably from all these, inasmuch as they enclose ethane, C²H⁶, and most probably propane, C³H⁸, and all the members of the paraffin series.

The whole of the cannel coals and jet contain the gases of the paraffin series, and oily matters apparently belonging thereto. Wigan cannels, with regard to the gases which they hold enclosed, occupy a position intermediate between steam and Scotch cannel; and Scotch cannel occupies a position intermediate between bituminous house coals and Wigan cannel. Thus, in the Wigan cannels, there is a large volume of gas, consisting for the most part of marsh-gas, with a low percentage of carbon dioxide and nitrogen, and, in these respects, closely allied to the steam coals. The Scotch cannels, on the other hand, contain but little gas, which consists almost entirely of carbon dioxide and nitrogen, similar to the bituminous class of house coals. Scotch cannel contains a small quantity of the higher hydrocarbon gases.

In the analysis of sample 4, the respective volumes of the contraction after explosion, carbon dioxide formed, and oxygen consumed, when compared with the volume, agree nearly with propane; it is possible, therefore, that CH⁴, C²H⁶, C³H⁸, may also be present. In sample No. 5, C²H⁶ and C³H⁸ agree nearly with the respective volumes above mentioned.

The gases from some of the cannel coals, when treated with fuming sulphuric acid, showed indications of olefine gases C^2H^2 , but it is probable that the loss in volume was due to the absorption of the vapour of the higher hydrocarbons, because, when the whole volume of combustible gas was exploded, the CO^2 formed, O consumed, and contraction due to explosion, did not agree with the calculated volume.

Negative results were obtained with ammonio-cuprous chloride, showing the absence of carbon monoxide.

Jet differs from the harder cannels by occluding only a small percentage of CO^2 and N, and also by containing a large percentage of C^2H^{2a+2} gas. The tube in which the gases were brought over by the pump contained one- or two-tenths of a c.c. of oily matter emitting the odour of paraffin.

Gases enclosed in Lignite and Mineral Resin from Bovey Heathfield in Devonshire (Thomas, *Chem. Soc. J.* 1877, ii. 146). The chemical composition of the lignites of this locality approaches that of some of the cannel and bituminous coals, but their structure differs greatly from that of the latter. Considerable differences are also found between the gases enclosed in lignite and in cannel. The greater portion of the gas enclosed, both in lignite and in cannel, consists indeed of CO^2 , but whereas cannel encloses gases, and apparently, also, liquid compounds of the paraffin series, the lignites contain olefine gases, C^2H^2 , and oily matters belonging to the aromatic series, in addition to appreciable quantities of carbon monoxide.

Lignites are much less stable than the coals of the carboniferous formation, decomposing in a vacuum at a much lower temperature—which in all those examined was below 200° —whereas the coals of the carboniferous era usually resist decomposition at 300° . Lignites are also very hygroscopic, the Bovey lignites especially so, reabsorbing from 10 to 12 per cent. of water in a few hours after being thoroughly desiccated.

The following table shows the composition of the gases evolved from leafy lignite from Bovey Heathfield at different temperatures. 100 grams of this lignite evolved 56.1 c.c. of gas at 60° , after prolonged heating for 12 days and nights, 90 per cent. being given off in the first two days, and the coal being apparently exhausted after the fourth day. The same lignite subsequently heated at 100° for 18 days, evolved 59.9 c.c. of gas. The temperature was then raised and maintained at 200° . At about 150° decomposition set in, and the surface of the mercury in the collecting tube became blackened by formation of mercury sulphide.

Composition of Gas in 100 parts.

	at 50°	at 100°	at 200°		
			1st portion	2nd portion	3rd portion
CO	87.25	89.53	88.39	82.06	71.13
CO^2	3.59	5.11	8.83	14.00	16.20
C^2H^2	—	0.83	2.32	0.97*	1.09
N	8.92	5.03	0.46	0.15	0.27
SH^2	—	—	†	2.82	5.85
O	0.24	—	—	—	—

The gas evolved at the higher temperatures smelt strongly of organo-sulphur compounds, and blackened the mercury in the tube of the Sprengel pump. When first collected it smelt of mercaptan, but after it was transferred to the apparatus for analysis, the odour of the more volatile sulphur-compounds disappeared, leaving unmistakable evidence of the presence of allyl sulphide.

A woody lignite from Bovey gave off at 100° a yellow sublimate consisting of small crystals of sulphur; it began to decompose at 183° , and at 200° gave off gas smelling of allyl sulphide, but containing only traces of hydrogen sulphide. The composition of the gas given off at 200° was:

CO^2	CO	C^2H^2	CH^4	C^2H^4	N
86.30*	7.41	2.08	3.34	0.53	0.34 = 100

The gas given off from the same lignite at 100° contained from 95.34 to 96.74 per cent. CO^2 .

* $0.49 C^2H^4 + 0.48 C^2H^2$.

† A small percentage of SH^2 , included in the CO^2 , was left undetermined by mistake.

A third lignite from the same locality gave off at 200°,

CO ²	CO	C ² H ⁴	H	SH ²	N	
91.68	7.12	0.41	trace	0.41	0.38	= 100

The same lignite yielded 94.98 per cent. CO² at 50°, and 97.8 per cent. at 100°.

The mineral resin (Hatchett's retinasphalt, v. 98) yielded but a small quantity of gas at 50°. At 100° in a vacuum, 100 grams of it yielded 21.4 c.c. of gas, containing in 100 pts.:

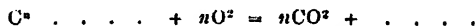
CO ²	CO	C ² H ⁴	N	O
88.24	7.90	0.47	3.16	0.23

Between 110° and 120° the resin began to melt and decompose, giving off a large quantity of sulphur-compounds, which attacked the mercury of the pump so strongly, that before the heat was raised to 160°, the gas could no longer be passed over. Previous to this, however, a quantity of gas was obtained equal to 180 c.c. per 100 grams of substance. This gas smelt somewhat like oil of amber, and contained in 100 pts.

CO ²	CO	C ² H ⁴	CH ⁴	C ² H ²	N	SH ²
78.88	7.82	2.67	8.05	1.86	0.31	0.41

COAL-GAS. Analyses of London coal gas have recently been made by T. S. Humpidge (*Chem. Soc. J.* 1876, i. 621). The samples of gas were collected in sealed tubes, the air of which was displaced by a rapid current of the gas. The mode of analysis employed was that described in Bunsen's Gasometry, in the chapter on Gas-analysis in Sutton's volumetric Analysis, and in the article Analysis of Gases, in this Dictionary (i. 268-289).

To distinguish the several hydrocarbons absorbed by fuming sulphuric acid, it was necessary to determine their carbon-density (or the value of n in the formula C ^{n} H ^{m}), as well as their percentage volume. This carbon-density is expressed by the volume of carbon dioxide produced by the combustion of one volume of the hydrocarbons, thus:—



and this CO² was found in the following manner:—

The heavy hydrocarbons in 100 vols. of the gas were first removed, and then the volume (A) of carbon dioxide, produced by the combustion of the residue, was determined. Then the volume of carbon dioxide (B) produced by the combustion of 100 volumes of the entire gas was determined. Now, if the percentage of the condensable hydrocarbons be represented by C, the volume of carbon dioxide produced by the combustion of one volume of these gases, in other words, their carbon-density, or the value of n in the formula C ^{n} H ^{m} , will be:—

$$\frac{B-A}{C}$$

Again, their equivalent in ethylene (i.e. where $n=2$), for 100 vols. of the gas is found by multiplying their percentage by half their carbon-density, that is $\frac{1}{2}Cd$, where d is the density; or substituting the value of d obtained above, the equivalent in ethylene is

$$\frac{B-A}{2d}$$

The results of the analyses made in May 1876, together with others made by Frankland in 1857, are given in the following tables (p. 536):

Frankland has shown (*Chem. Soc. J.* v. 39) that marsh-gas and carbon monoxide contribute nothing to the illuminating power of a gas, being in fact as much without illuminating power as hydrogen. In the case of canal gases the illuminating power may be calculated from the equivalent of ethylene; but ordinary coal-gas contains traces of other hydrocarbons, possibly paraffins, (C²H⁶, C³H⁸, C⁴H¹⁰), not condensable by fuming sulphuric acid; these, however, have but a slight influence on the illuminating power.

On comparing the two sets of analyses of the London gas, made at an interval of twenty-five years, it will be seen that the real illuminating power of the gas has not increased, and that in the case of canal gas it has actually diminished.

COMPOSITION OF LONDON COAL-GAS. TABLE I.—*Determinations, July 1851 (Frankland).*

	CO						Carbon-density	Equivalent in C ² H ⁴	
City Co., taken at Blackfriars (Newcastle Coal).	0.53			47.60	7.32	41.50	3.05	4.57	6.97
Great Central Co., taken at office, Coleman-street, 3 miles from works (Newcastle Coal and Cannel).	0.28	0.44	1.80	51.24	7.40	35.28	3.56	4.05	7.21
Western Co., taken at works, Paddington (Newcastle Cannel).	0.13	0.43	1.51	25.82	7.85	51.20	13.06	3.52	22.98
Imperial, taken $\frac{1}{2}$ mile from Battle Bridge Works.	0.29	1.20	5.01	41.15	8.02	40.66	3.67	3.35	6.15
Chartered, taken $\frac{1}{2}$ mile from works, Brick Lane.	None	0.08	0.38	51.81	8.95	35.25	3.53	4.36	7.70

TABLE II.—*Determinations, May 1876 (Humpidge).*

	CO ¹	O	N	H	CO	CH ⁴	C ² H ⁴	Carbon-density	Equivalent in C ² H ⁴
1. <i>Imperial Co.</i> , Crane Grove, Holloway Road, 10.30 p.m.	None	1.91	9.73	40.82	6.79	36.57	4.18	3.81	7.96
2. <i>Chartered Co.</i> , Beckton Testing House . . noon	None	Traces	3.48	50.59	3.13	38.39	4.41	3.56	7.85
3. <i>Chartered Co.</i> , Mr. Heisch's office . . 11.30 a.m.	None	0.22	4.98	50.28	4.37	36.95	3.22	3.94	6.34
4. <i>Chartered Co.</i> , Mr. Heisch's office . . 9.30 p.m.	None	0.60	3.22	50.62	6.96	34.49	4.11	3.16	6.49
5. <i>Chartered Co.</i> , Royal College of Chemistry . noon	Traces	0.26	4.93	50.68	3.98	35.89	4.08	3.26	6.65
6. <i>Chartered Co.</i> , Royal College of Chemistry . 9 p.m.	Traces	0.40	5.40	43.99	6.42	30.36	4.12	3.31	6.82
7. <i>House of Parliament</i> , (Cannel) 7 p.m.	None	None	2.71	41.72	4.98	41.88	8.72	4.51	19.66

Berthelot (*Compt. rend.* lxxxii. 871, 927) has examined the coal-gas of Paris, and finds it to contain benzene, propylene, allylene, crotonylene, and terene (C^4H^6). The benzene was determined by collecting the gas over water in a vessel which was closed, when full, by a cork supporting a tube of 1 c.c. capacity, filled with fuming nitric acid. On shaking the apparatus this tube was broken, and the nitric acid acted upon the benzene, converting it into nitrobenzene; the excess of nitrous vapour was then removed by potash, and the volume of the residual gas determined. The proportion of benzene-vapour in the gas was thus found to be from 3 to 3.5 volumes per cent. The proportion of the gas absorbed by bromine did not exceed 3.5 volumes per cent.: hence Berthelot concludes that the quantities of acetylene and ethylene in the gas do not amount to more than $\frac{3000}{3000}$ to $\frac{1}{3000}$. For the estimation of butylene, &c., the gas was passed through sulphuric acid diluted with an equal volume of water, and then over pumice soaked in strong sulphuric acid. In the diluted acid, a quantity of tarry liquid (b.p. 360° – 400°) separated, amounting to 4 or 5 grams for 100 cubic meters of the gas. The watery liquid itself contained about 0.25 gram of acetone, which Berthelot attributes to the hydration of allylene contained in the gas.

In the vessel containing the concentrated sulphuric acid, a supernatant layer of hydrocarbons was formed, together with sulphuric acid more or less altered. On treating this liquid with water, a quantity (25 grams) of viscid hydrocarbons boiling at 300° to 400° was separated, and sulphurous acid was evolved. The water itself had taken up isopropyl alcohol (0.5 gram). From the supernatant layer of hydrocarbons the following were separated:

Benzene	2 per cent.	
Mesitylene	5 "	(b. p. 160°)
Cymene	20 "	(" 180°)
Tricrotonylene ($C^{12}H^{18}$)	30 "	(" 220° – 240°)
Colophene ($C^{14}H^{24}$)	32 "	(" 300° – 320°)
Residue	5 "	(" 320°)
Loss	6 "	

Berthelot regards these hydrocarbons, with the exception of benzene, as condensation-products produced by the action of the sulphuric acid on volatile hydrocarbons contained in the gas; mesitylene by the union of 3 mol. allylene; cymene by partial oxidation of terene (C^6H^{10}), which again may be supposed to be formed from 2 mols. of terene or propylacetylene (C^6H^8); tricrotonylene may be regarded as a condensation-product of crotonylene, and colophene as similarly formed from terene.

From the preceding data the portion of the gas absorbable by bromine may be supposed to contain in a million parts by volume:

Vapour of benzene	C^6H^6	30,000 to 35,000
Acetylene	C^2H^2	1,000
Ethylene	C^2H^4	1,000 to 2,000
Propylene	C^3H^6	2.5
Allylene	C^3H^4	8
Butylene, &c.	C^4H^8	traces
Crotonylene	C^4H^8	31
Terene	C^6H^{10}	42
Nearly non-volatile condensation-products	—	83
Diacetylene and analogous compounds	—	15

These hydrocarbons may be supposed to be formed partly by the destructive distillation of the coal itself, partly from the so-called fundamental hydrocarbons, acetylene, ethylene, ethane, and methane.

Dittmar (*Chem. News*, xxxiv. 146) has analysed the gas of Edinburgh, and finds, in accordance with the results of the analysis of coal-gas from various sources by Bunsen, Landolt, and others, that this gas contains but an extremely small quantity of benzene, and scarcely a trace of any heavy hydrocarbon except ethylene. He shows that the liquid bromides separated by bromine from coal-gas, are almost wholly decomposed by alcoholic potash, and, consequently, that only a minute proportion of them can consist of benzene bromide, which is not decomposed by alcoholic potash.* On the other hand, he observes that benzene, even in small quantity, may increase the luminosity of a gas much more than ethylene; for a mixture of 3 vol. ethylene with

* The non-occurrence of benzene bromide among the liquid bromides obtained from coal-gas, does not prove the absence of benzene in the gas itself, inasmuch as benzene does not unite with bromine, for the influence of bright sunshine.

3 vol. Hydrogen burns with an almost non-luminous flame, whereas hydrogen mixed with only 3 per cent. of benzene-vapour burns with a very bright flame.

On the Analysis of Coal-gas, see further Berthelot (*Compt. rend.* lxxxiii. 1266; lxxxiv. 670; *Chem. Soc. J.* 1877, i. 743; ii. 447).

The following comparative statement of the composition of coal-gas, in various localities, is given by F. Chandler (*American Chemist*, vi. 286):

	Heidelberg	Bonn	Chemnitz	London	
				Ordinary coal-gas	Cannel gas
Hydrogen	44.00	39.80	51.29	46.00	27.70
Marsh-gas	38.40	43.12	36.45	39.50	50.00
Carbon Monoxide	5.73	4.66	4.45	7.50	6.80
Heavy Hydrocarbons	7.27	4.75	4.91	3.80	13.00
Nitrogen	4.23	4.65	1.41	0.50	0.40
Carbon Dioxide	0.37	3.02	1.08	—	0.10
Water-vapour	—	—	—	2.00	2.00

An elaborate paper on the composition and properties of coal-gas, with reference to its technical value, based especially on an examination of the Berlin gas, has been published by Tiefrunk (*Dingl. pol. J.* ccxxii. 466, 558; *Jahresb. f. Chem.* 1876, 1158).

Purification of Coal-gas. 1. *From Hydrogen Sulphide and Ammonia.*—The hydrogen sulphide present in crude coal-gas is now generally removed by means of ferric hydrate. Now this hydrate, technically known as 'oxide,' becomes 'spent,' after having been used some twenty or thirty times, and is then sold to the vitriol-maker. To prevent this deterioration, Harcourt and Fison have devised a process, which at the same time removes the ammonia from the gas without the use of 'scrubbers,' and enables the gas manufacturer to obtain sulphur containing but little impurity, and ammonia in the form of sulphate. The method, which is continuous, consists essentially in moistening the oxide with a solution of ferric sulphate containing sulphuric acid, before introducing it into the purifier. The ammonia of the gas entering the purifier is converted into sulphate, and the ferric oxide formed fixes the sulphur. The oxide, after removal from the purifier, is washed with water, which removes the ammonium sulphate, and a portion of the residue is boiled with dilute sulphuric acid, which dissolves ferric oxide for a fresh charge, and leaves the sulphur. In practice it is found best to proceed thus: the oxide taken from the purifier is washed with water, and the liquor evaporated to obtain ammonium sulphate, a little sulphuric acid being first added. The oxide is then boiled successively with four dilute solutions of sulphuric acid, *a, b, c, d*, each weaker than the preceding, and finally washed with water. Solution *a* is used in moistening a fresh charge of oxide before it enters the purifier. Solution *b* becomes solution *a* when more oxide is ready for extraction. Solution *c* then takes the place of *b*, and *d* of *c*, the water used at the end of the previous treatment becoming the solution *d* of the new one (*Chem. News*, xxviii. 175).

2. *From Carbon Disulphide.*—The vapour of this compound is not removed from coal-gas by the ordinary method of purification from sulphuretted hydrogen, and, consequently, when the gas is burned, sulphurous anhydride is produced. It may, however, be removed by passing the gas (either before or after purification) through an iron tube filled with iron turnings, and heated to redness. The sulphur of the carbon sulphide is, in this manner, converted into sulphuretted hydrogen, and the total amount of carbon sulphide is so far reduced, that the gas, after purification from sulphuretted hydrogen, contains only 5 or 6 grains of sulphur instead of 30 grains in 100 cubic feet.

A somewhat greater reduction in the amount of sulphur is obtained by heating the gas after, instead of before purification, and purifying it a second time. When coal-gas is passed slowly over red-hot iron, a soft, black, carbonaceous deposit is formed, and the gas is deprived of a portion of its carbon; but if the gas be passed through more rapidly, no such deposition takes place, although the time of contact with the heated surface is sufficient to effect the conversion of the carbon sulphide into sulphuretted hydrogen. In the latter case, no diminution in the illuminating power of the gas takes place; on the contrary, if the heat be raised to bright redness,

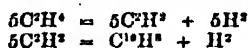
a slight yet perceptible increase in the illuminating power may be observed (A. Vernon Harcourt, *Chem. Soc. J.* 1873, 299).

Effect of Heat on Coal-gas. Blochmann (*Liebig's Annalen*, clxxiii. 187) has studied the alterations produced in coal-gas, by passing it through a porcelain tube heated to nearly 1,000°, the temperature being estimated by means of small pieces of metals and alloys of known melting points. The following table shows the composition of the gas before and after the experiment :

	Before	After
Hydrogen	49.57	61.96
Marsh-gas	36.92	30.49
Carbon Monoxide	5.63	5.26
Ethylene	3.92	1.26
Butylene	2.99	0.17
Nitrogen	0.97	0.86
	100.00	100.00
Acetylene	0.06	6.11

The increase in the amount of hydrogen, after passing through the heated tube, arises from the decomposition of the hydrocarbons, and, in fact, the tube was found to be lined with a deposit of carbon.

The glass tube leading from the heated porcelain tube contained a deposit of naphthalene, the production of which may be explained by the equations :



Effect of Caoutchouc Tubes on the Illuminating Power of Coal-gas. Zulkowsky (*Deut. Chem. Ges. Ber.* v. 759) has measured this effect by enclosing three mineralised caoutchouc tubes, having a total length of 4.26 meters, in three glass tubes communicating with each other, and with the gas-meter of a photometrical apparatus. The gas-meter, which was so regulated as to furnish 5 cubic feet in an hour, was then supplied alternately with coal-gas which had passed over the caoutchouc, or with ordinary coal-gas, and the illuminating powers were estimated :

Illuminating Power of Coal-gas.

	Directly supplied	Passed over caoutchouc	Directly supplied	Passed over caoutchouc	Directly supplied
1st series	13.2	10.7	12.9	—	—
2nd „	12.2	9.2	12.1	—	—
3rd „	—	7.8	11.2	7.5	11.3
4th „	—	9.8	11.6	9.9	12.0

The diminution of the illuminating power was thus proved to be due not to the diffusion through the caoutchouc, but to the absorption of some of the light-giving constituents by that substance. To determine the amount of this absorption, some pieces of black caoutchouc were dried in a vacuum over sulphuric acid, and then placed in a chloride of calcium tube, through which perfectly dry coal gas was passed. The increase of weight after intervals of six hours is given in the following table :—

The weight of the caoutchouc tube was		Increase of weight
At the commencement		11.889
After 6 hours		12.001
12 „		12.125
18 „		12.253
24 „		12.369
30 „		12.505
41 „		12.691
47 „		12.745
53 „		12.816
59 „		12.873

Total

1.024

When the caoutchouc tubes, after several days' exposure to the current of gas, were transferred to a vacuum over sulphuric acid, the manometer rose slowly and the sulphuric acid turned black, showing that the absorbed gaseous constituents were given off again.

As the same effect must be produced by diffusion when the caoutchouc tubes are exposed to the air, it is easy to see why tubes which have been in use for a long time diminish the illuminating power quite as much as new ones.

The diminution of volume caused by the caoutchouc was found to be very small, amounting to 1.1 per cent. only, but was much greater in the case of coal-gas which had been passed over benzene, evidently because vapours are more easily absorbed than permanent gases.

Products of Combustion. On the products of the combustion of coal-gas in the non-luminous flame of the Bunsen burner, and of its imperfect combustion in the feeble, strong-smelling flame which burns at the bottom of the tube of the same burner, when the upward flow of the gas is not strong enough to keep up the combustion at the top, see the article *FLAME* in this volume.

Products formed by the Combustion of the Impurities in Coal-gas.—C. R. Tichborne (*Chem. News*, xxx. 4) finds that the ammonia and aniline in coal-gas are converted by oxidation into nitrous acid, or one of the lower oxides of nitrogen.

The products formed by the combustion of the sulphur are determined to a great extent by the composition of the gas. In gas of high illuminating power—rich, therefore, in heavy hydrocarbons—the sulphur burns to sulphurous acid, but in gas of low illuminating power it burns to sulphuric acid.

From experiments by Heisch, W. C. Young and Wigner (*Analyst*, Nov. 1877, pp. 133, 135, and 138), it appears that the sulphur in ordinary coal-gas is converted by burning, for the most part, if not wholly, into sulphuric acid. Heisch found the air of a small, badly ventilated room in which coal-gas was burned, to be free from sulphurous acid; but by cooling the air and examining the moisture condensed, he found 0.3 grain of H_2SO_4 per 100 cubic feet of gas burnt, the gas containing 20 grains of sulphur per 100 cubic feet. In a similar experiment with gas containing 5.5 grains of sulphur per 100 cubic feet, only 0.056 grain of H_2SO_4 was found. The production of sulphuric acid, therefore, increases more rapidly than the actual amount of sulphur. —Young has demonstrated by numerous experiments the presence of sulphuric acid in the air of a very well-ventilated room in which coal-gas was burnt. Moist linen, paper, cards, &c., placed in different parts of the room, and washed after the combustion had proceeded for a certain time, always yielded washings containing sulphuric acid. A deposit formed on the inner surface of the chimney of a 'Sugg's London Argand' was found to consist of stannic sulphate; hence sulphuric acid was produced close to the base of the flame, where combustion is supposed to be but partially complete. —Wigner examined the air which escaped from an artificially ventilated room in which coal-gas was burned; no sulphurous acid was detected, but quantities of sulphuric acid were obtained, representing 22 to 62 per cent. of the total sulphur in the gas.

Effect of Coal-gas on Plants. Experiments have been made in the Botanic Garden at Berlin, to determine the effect produced upon the roots of trees and shrubs by gas escaping from pipes into the soil. A maple and a lime-tree, $3\frac{1}{2}$ and $5\frac{1}{2}$ feet in diameter, were treated daily for six months, beginning in July, with 100 cubic feet of gas, introduced $2\frac{1}{2}$ feet under the surface of the soil, and about 3 or 4 feet from the trees; they began to look sickly after a month's exposure to the action of the gas; the maple died in the following spring, and the lime in the summer. An examination of the roots showed that the poisoning begins at the growing ends of the roots, and that the bark of the roots is not acted on. In another experiment, 25 cubic feet of gas were daily passed into a plot of ground having a surface of 144 square feet, and on which twelve young trees had been growing for a year and a half; the trees showed signs of poisoning in a week's time, where the surface of the soil had been firmly stamped down, and in a month they had all lost their leaves (Späth and Meyer, *Annalen der Landwirtschaft*, 1872, 764).

Further experiments showed that the same quantity of gas applied during the winter has a much less injurious effect than when applied during the period of growth. It was found that when 0.0165 cubic meter ($6\frac{1}{2}$ cubic feet) of gas were passed daily during the spring into a plot of 14.19 square meters (163 square feet) by 0.781 meter ($2\frac{1}{2}$ feet) deep, on which 17 trees were growing, six of the trees were dead at the end of seven weeks, and after 11 weeks only two were living, and these in a sickly state. Lime and elm trees appear to resist the injurious action longest (*Landw. Versuchs-Stationen*, xvi. 336).

J. Boehm (*Chem. Centr.* 1873, 755) found that cuttings of willow, the lower ends of which were placed in flasks containing a little water, and filled with coal-gas, developed only short roots, and that the buds on the upper parts died shortly after unfolding in the air. Of ten plants in pots (varieties of fuchsia and salvia), amongst the roots of which coal-gas was conducted through openings in the bottoms of the pots, seven died in four months. To show that the plants were killed, not by the direct action of the gas, but in consequence of the poisoning of the soil, several experiments were made with earth through which coal-gas had passed for two or three hours daily for two and a-half years. The rootlets of seeds sown in this soil remained very short, and soon rotted. A plant of *Dracæna* was re-potted in the soil; in ten days the leaves dried up and the roots died. Boehm thinks that these results sufficiently account for the fact that trees planted near gas-pipes in streets so often die; and recommends the enclosing of gas-pipes in wider tubes, having openings to the air, and through which currents could be maintained by artificial means. Such a plan is still more to be recommended on hygienic grounds, since it has been shown by Pettenkofer that infiltration of coal-gas through the soil takes place even into houses not supplied with gas.

COBALT. On the Magnetic properties of Metallic Cobalt, and the Alteration of its Molecular structure by Magnetisation, see *MAGNETISM*.

On the Spectra of certain Cobalt-compounds in Blowpipe Chemistry, see Horner (*Chem. News*, 1873, i. 241).

Reaction with Hydrogen.—A thin electrolytically deposited plate of cobalt is capable of occluding hydrogen in the same manner as palladium (Böttger, *J. pr. Chem.* [2], ix. 193).

Precipitation.—W. Gibbs (*Chem. News*, 1873, ii. 51) describes a modification of Wöhler's method of precipitating cobalt from a solution of potassium cobaltcyanide by mercuric nitrate, which consists in precipitating from a hot solution, and then boiling the precipitate for some minutes with mercuric oxide. The granular, crystalline, easily-washed, precipitate thus obtained is ignited in contact with the air, and finally reduced in a current of hydrogen gas.

When *magnesium* is immersed in a solution of cobalt chloride, hydrogen is evolved, and a green precipitate of cobaltous oxide is formed, while magnesium chloride remains in solution:



(Kern, *Chem. News*, xxxii. 309).

According to Lecoq de Boisbaudran (*Compt. rend.* lxxxii. 1100), metallic cobalt is precipitated from its solutions by *zinc*, provided the solution is not too acid, and contains also a metal, such as copper or lead, which is easily reduced by zinc.

Electrodeposition.—According to Böttger (*Chem. Centr.* 1876, 640), a bright coating of cobalt may be deposited on brass or copper from a solution of the chloride of cobalt and ammonium, subjected to the current of two Bunsen's elements. The solution is best prepared by dissolving 40 grams of crystallised cobalt chloride and 20 grams of ammonium chloride in 100 c.c. of distilled water, and adding 20 c.c. of aqueous ammonia.

On the Estimation of Cobalt by Electrodeposition, see *Dingl. pol. J.* cccxxx. 66; *Chem. Soc. J.* 1877, ii. 926.

Estimation by Precipitation as Oxalate.—A neutral concentrated solution of a cobalt salt is treated with a solution of potassium oxalate (1 : 6) and strong acetic acid is added, as long as a precipitate is formed. This precipitate is warmed on a water-bath, collected on a filter, and washed with strong acetic acid, or a mixture of equal volumes of strong acetic acid, alcohol (95 per cent.), and water, and then ignited in the usual manner (*Classen, Deut. Chem. Ges. Ber.* x. 1316).

A similar method of precipitation may be applied to the separation of cobalt (and of nickel) from arsenic, instead of the use of hydrogen sulphide for precipitating the latter. The arsenical ore is dissolved in aqua regia, any great excess of acid is driven off by evaporation, and the boiling-hot solution is precipitated with sodium carbonate. The precipitate after washing is treated, while still moist, with excess of a strong solution of oxalic acid, whereby the cobalt and nickel are converted into oxalates, while the whole of the arsenic passes into solution, together with any ferric oxide that may be present. The mixed oxalates, after thorough washing, may be separated by means of ammonia. If copper be present, it may be separated by means of finely divided iron, before the precipitation with sodium carbonate (Wöhler, *Deut. Chem. Ges. Ber.* x. 646).

Separation from Nickel.—This separation may be effected by adding a solution of potassium selenite to a cold, slightly acid solution of the two metals, whereby they

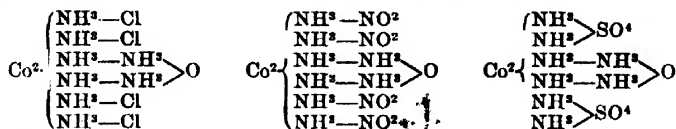
are precipitated together as xanthates, and treating the precipitate, after decantation of the supernatant liquid, with aqueous ammonia diluted with an equal bulk of water, which immediately dissolves the xanthate of nickel, leaving the cobalt salt undissolved (Phippsen, *Chem. News*, xxxv. 270; xxxvi. 156).

Separation from Zinc.—This metal also forms an easily soluble xanthate, and may, therefore, be separated from cobalt in the same manner as nickel (Phippsen). Another mode of separation, depending on the volatility of zinc chloride, is given by Fresenius (*Zeitschr. Anal. Chem.* 1873, 66). The solution of the two metals in hydrochloric acid is mixed with a sufficient quantity of sal-ammoniac, and evaporated to dryness, and the dry residue is cautiously heated till all the sal-ammoniac, and with it all the zinc chloride, is volatilised.

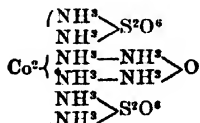
On the Manufacture of Large Castings of Cobalt, see Winkler (*Dingl. pol. J.* cxxxii. 175; *Chem. Soc. J.* 1877, i. 238).

On a Native Hydroxide of Cobalt and Nickel, see HEUBACHITE.

Isacial Compounds of Cobalt (W. Gibbs, *Amer. J. of Sci.* [3], viii. 189 and 296). The octammonio chloride, nitrate, and sulphate (fusocobaltic salts), described by Frémy (i. 1051; 1st *Suppl.* 477) may be represented by the following formulæ:



and Künzel's hyposulphite (thiosulphate) may also be viewed as belonging to this series, thus:



By the action of ammonium nitrite on neutral salts of cobalt, Erdmann obtained the salt $\text{Co}^2(\text{NO}^2)^4(\text{NH}^3)^4 + 2(\text{NH}^3)\text{NO}^2$. Sadtler, by the action of ammonium nitrite on acid solutions of cobaltic chloride, obtained two salts having the formulæ $\text{Co}^2(\text{NO}^2)^{10}(\text{NH}^3)^4 + 2\text{H}^2\text{O}$ and $\text{Co}^2(\text{NO}^2)^{12}(\text{NH}^3)^6 + 2\text{H}^2\text{O}$, respectively, and Gibbs by acting on cobaltic chloride with ammonia and potassium nitrite, obtained the salt $\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^4$, which may be regarded as the nitrite of the hexamine, $\text{Co}^2(\text{NH}^3)^4$. No other members of the same series have, however, been obtained from it, but the dichrocobalt chloride, $\text{Co}^2(\text{NH}^3)^4(\text{Cl}^4) + 2\text{H}^2\text{O}$, of Fr. Rose, and Künzel's sulphite, $\text{Co}^2(\text{NH}^3)^4(\text{SO}^3)^4 + 2\text{H}^2\text{O}$, may be regarded as analogous compounds.

In the formation of the hexamine nitrite, and also of the two salts described by Sadtler, an absorption of atmospheric oxygen occurs. On repeating Erdmann's experiment for the production of the hexamine nitrite, small quantities of that salt were formed, but the chief products were salts of xanthocobalt. The solution remaining in this reaction was found to contain a salt of xanthocobalt and a corresponding salt of the octamine series. These experiments show that the action of ammonium nitrite on salts of cobalt in presence of free acid is very complex, not less than six classes of salts being formed, of which two belong to basic series, three may be viewed as ammonium salts, and one is probably a term of a hexamine series.

Erdmann's ammonia nitrites present the only known instances in which cobalt, by combination with ammonia and nitroxyl, forms an electro-negative radicle. The compound $\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^4$ may be viewed as existing in combination with two atoms of a monatomic radicle, exactly as the compound $\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^4$ combines with two atoms of chlorine. The structural formulæ of these two salts may be written:



Thallium salt.—The potassium salt forms with thallous nitrate a sherry-coloured precipitate, which, on recrystallisation, gives well-defined prismatic crystals, having apparently the same form as the corresponding potassium and ammonium salts.

Mercurous salt, $\text{Co}^2(\text{NH}_3)_4(\text{NO}_3)_2\text{Hg}^2$.—A solution of potassic ammonia-cobalt-nitrite forms with mercurous nitrate, a crystalline, orange-coloured precipitate, soluble with partial decomposition in boiling water, from which it does not crystallise well.

With salts of cobalt, nickel, barium, and copper, the potassium salt gives no precipitates. With lead acetate, after some time, a crystalline brown-orange precipitate is formed, soluble in hot water, with partial decomposition. With silver, the same effect occurs, but in small quantities the precipitate may be dissolved without decomposition.

Compounds of ammonia-cobalt-nitrate with barium, strontium, &c., are readily formed by digesting the metallic chlorides with a solution of the silver salt. They are pale orange-yellow soluble bodies, which have not been fully examined.

The potassium salt gives crystalline precipitates with various alkaloïds, especially strychnine, brucine, &c. They are soluble in hot water, and may be crystallised therefrom without sensible decomposition. The potassium salt gives with salts of aniline a bright yellow precipitate, which is immediately decomposed, with liberation of phenol; it also yields crystalline precipitates with salts of croceocobalt, xanthocobalt, and luteocobalt. It does not combine with iodine.

DECAAMMONIC COMPOUNDS.—*Xanthocobaltic Salts* are formed by the action of red nitrous vapours upon solutions of cobalt salts in presence of an excess of ammonia, and are almost the only products of the reaction. When cobalt chloride was used, crystals of the chloronitrate, $\text{Co}^2(\text{NH}_3)_6(\text{NO}_3)_2(\text{NO}_2)_2\text{Cl}^2$, were occasionally detected; and in one instance in which cobalt sulphate was used, mixed with such an excess of ammonium sulphate that ammonia produced no precipitate, a considerable proportion of Erdmann's salt, $\text{Co}^2(\text{NH}_3)_6(\text{NO}_3)_4$, was produced. The solutions, after the action of the red vapours, contain small quantities of ammonia-cobalt-nitrate of ammonium, with ammonium nitrate and nitrite.

Xanthocobaltic salts are formed in large quantities, together with a little of the octamine nitrate, by the action of a mixture of potassium nitrite and ammonia upon cobalt nitrate in presence of air, whereas when the same mixture acts under similar conditions upon cobalt sulphate, the xanthocobaltic salt is the only product. No plausible explanation has yet been found for this difference of action.

If a mixture of cobaltic nitrate, ammonia, and ammonium nitrite be placed in a tightly-corked bottle, no reaction occurs even after some days; but if a little peroxide of lead be added, this oxide is reduced in a few hours, and large crystals of xanthocobaltic nitrate are formed. It appears probable that, in the action of the nitrous vapours upon cobalt salts in presence of ammonia, the xanthocobalt formed does not result from the direct union of the cobalt salt with ammonia and nitroxyl, but that ammonium nitrite is at first formed, and that the oxygen necessary for the completion of the reaction is derived from the mixture of nitrogen oxides which make up the red vapours.

Xanthocobaltic salts are always formed when salts of purpureo- or roseo-cobalt are heated, or digested in the cold, with alkaline nitrites.

On treating a hot solution of purpureo-cobaltic chloride acidified with acetic acid with hot potassium or sodium nitrite, an anhydrous salt having the composition $\text{Co}^2(\text{NH}_3)_6(\text{NO}_3)_2(\text{NO}_2)_2\text{Cl}^2$ is obtained. It is a *nitroso-chloro-nitrate*, and might be supposed to belong to the α -decamine (purpureo-cobalt) series, but is more probably the chloro-nitrate of xanthocobalt, as it yields, with various reagents, precipitates of xanthocobaltic salts.

Gold salt.—On adding an excess of sodio-auric chloride to a solution of the chloronitrate, prismatic wine-yellow crystals are formed, having the composition $\text{Co}^2(\text{NH}_3)_6(\text{NO}_3)_2(\text{NO}_2)_2\text{Cl}^2 + \text{AuCl}^3$. On boiling, the salt is decomposed, with deposition of metallic gold.

Platinum salt.—Platinic chloride precipitates the chloro-nitrate almost immediately in wine-yellow needles which have the composition $\text{Co}^2(\text{NH}_3)_6(\text{NO}_3)_2(\text{NO}_2)_2\text{Cl}^2 + 2\text{PtCl}^4$. They yielded no water when heated to 140° .

Bromo-nitrate.—Solutions of xanthocobaltic bromide and of the nitrate of the same base mixed in the proportion of one molecule of each, yielded after some hours a dark crystalline body having, after two crystallisations, the composition $\text{Co}^2(\text{NH}_3)_6(\text{NO}_3)_2(\text{NO}_2)_2\text{Br}^2$. The salt is much less stable than the chloro-nitrate, and decomposes on further crystallisation.

The endeavour to form a double salt of xanthocobaltic nitrate with purpureocobaltic chloride, by mixing their solutions in molecular proportions, was only partially suc-

cessful; but it seems established that such a double salt may exist. Experiments, with the object of forming several other double salts by similar processes, led to no definite results.

The above-described nitroso-chloro-nitrate appears to be the body at one time regarded by Gibbs as the chloride of a special radicle, the so-called *flavocobalt*. It

Cooke's measurements of the crystals of the nitrate and chloride respectively, that the former belongs to the dimetric, and the latter to the trimetric system.

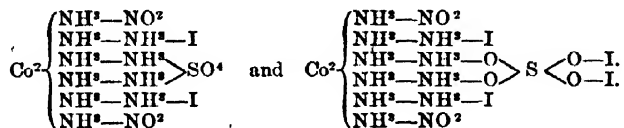
Salts of xanthocobalt are formed by the action of Fischer's salt, $\text{Co}^2(\text{NO}^2)^{12}\text{K}^6$, upon salts of roseo- or purpureo-cobalt. Thus, if Fischer's salt be added to a boiling acidified solution of purpureo-cobaltic chloride, the liquid on cooling deposits crystals of xanthocobaltic chloride, the complementary products being potassium chloride, cobalt nitrite, and nitrogen tetroxide.

The *chromate*, $\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2(\text{NO}^2)^2(\text{CrO}^4)^2 \cdot 2\text{H}^2\text{O}$, is formed by the addition of normal potassium chromate to xanthocobaltic nitrate. It is but slightly soluble in hot or cold water, and loses only 0.68 per cent. of water at 145° .

From this salt the chloride and sulphate of xanthocobalt are most easily produced, the former by adding barium chloride so long as barium chromate is precipitated, the latter from the former by double decomposition with silver sulphate. The *dichromate*, $\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2(\text{Cr}^2\text{O}^7)^2$, is produced by the addition of potassium dichromate to strong solutions of xanthocobaltic nitrate. It is easily soluble in hot water, from which it crystallises on cooling.

Iodosulphates.—In solutions of xanthocobaltic nitrate, potassium iodide yields, after some time, pale brown-yellow crystals of the iodide, $\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2\text{I}^4$. If iodine in solution of potassium iodide be used, no periodide is formed, as is the case with the iodide of the hexamine series; but iodine is precipitated in crystals.

With xanthocobaltic sulphate, potassium iodide yields a precipitate of yellow-brown needles, crystallising in larger prisms after re-dissolution. Their formula was found to be $\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2\text{SO}^4\text{I}^2 \cdot 2\text{H}^2\text{O}$. The xanthocobaltic sulphate yields with iodine in solution in potassium iodide, ruby-red crystals, which are decomposed by boiling water and cannot be recrystallised. The analytical numbers obtained, though not agreeing very closely with those calculated, showed the formula to be $\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2\text{SO}^4\text{I}^4$. The structural formulæ of the two salts may be thus written:—



An attempt to produce a platinochloride of chlorosulpho-xanthocobalt by adding sodio-platinic chloride to xanthocobalt sulphate was not successful.

Xanthocobaltic Nitrite.—By boiling silver nitrite with purpureocobaltic chloride, and evaporating the filtered solution, two salts, one in scales, and one in octohedral crystals, were formed. The former was found to be the *ammonia-cobalt-nitrite of silver*, $\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2\text{Ag}^2$; the other (which is better produced by decomposing roseocobaltic sulphate with barium nitrite, and evaporating the filtered liquor), was found to be the *xanthocobaltic nitrite*, $\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2 \cdot 4\text{H}^2\text{O}$. From its empirical formula it might be regarded as purpureo- or roseocobaltic nitrite, but as it gives all the reactions of xanthocobalt, it is more probably the normal nitrite of the xantho-series, $\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2(\text{NO}^2)^2 \cdot 4\text{H}^2\text{O}$.

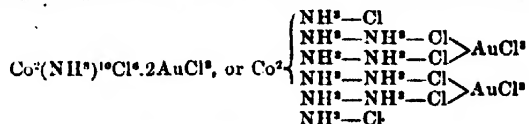
Ammonia-cobalt-nitrite of Xanthocobalt.—By the addition of a solution of potassic ammonia-cobalt nitrite to a solution of xanthocobaltic nitrate, a crystalline precipitate is formed, which may be recrystallised without decomposition. Its solutions give the reactions of xanthocobalt, and its formula is $\{\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2\} \{\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2\}^2$. It is metameric with the corresponding salt of the hexamine series, and with Erdmann's $\text{Co}^2(\text{NH}^3)^6(\text{NO}^2)^6$, of which it is, numerically, the threefold multiple. On standing for some time in solution, it decomposes, yielding a considerable quantity of cobalt nitrate.

Xanthocobaltic Oxalate.—This salt has been erroneously supposed to contain $2\frac{1}{2}$ mol. H^2O . It is really anhydrous, the analyses corresponding with the formula $\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2(\text{C}^2\text{O}^4)^2$.

The following is a list of the salts of the xantho-series at present known :

Chloride	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2\text{Cl}^4$
Bromide	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2\text{Br}^4$
Iodide	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2\text{I}^4$
Nitrate	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^4(\text{NO}^3)^4$
Nitrite	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2(\text{NO}^2)^2 + 4\text{H}^2\text{O}$
Sulphate	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2(\text{SO}^4)^2$
Iodosulphate	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2(\text{SO}^4)^2 + 2\text{H}^2\text{O}$
Hyperiodosulphate	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2\text{SO}^4\text{I}^4$
Aurochloride	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2\text{Cl}^4.2\text{AuCl}^3 + \text{H}^2\text{O}$
Platinochloride	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2\text{Cl}^4.\text{PtCl}^4 + \text{H}^2\text{O}$
Mercurio-chloride	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2\text{Cl}^4.4\text{HgCl}^2 + \text{H}^2\text{O}$
Oxalate	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2(\text{C}^2\text{O}^4)^2$
Chromate	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2(\text{CrO}^4)^2 + 2\text{H}^2\text{O}$
Dichromate	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2(\text{Cr}^2\text{O}^7)^2$
Ammonio-cobalt-nitrate	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2\{\text{Co}^2\text{NH}^3\}^4(\text{NO}^3)^4$
Ferrocyanide	$\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^2\text{FeCy}^6 + 6\text{H}^2\text{O}$

Purpureocobaltic Salts.—The *aurochloride* is obtained by addition of auro-sodic chloride to purpureocobaltic chloride containing free hydrochloric acid. After some hours, flat, prismatic, ruby-red crystals are deposited having a violet lustre, and exhibiting, after standing, a superficial reduction of gold. The formula of the salt is :



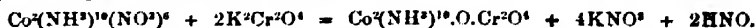
from which it appears to be unsaturated, similar salts with 4 and 6 atoms of auric chloride being possible.

Mercurio-chloride.—On the addition of an excess of mercuric chloride to a solution of purpureocobaltic chloride, a dull red salt separates, slightly soluble in cold, more so in hot water, especially if free hydrochloric acid is present. Its formula is $\text{Co}^2(\text{NH}^3)^4(\text{Cl}^4).6\text{HgCl}^2$. If the purpureocobaltic chloride is in excess, or if the salts are mixed in atomic proportions, a salt separates in violet prismatic crystals, which have the formula $\text{Co}^2(\text{NH}^3)^4\text{Cl}^4.4\text{HgCl}^2$. The salt with 6 atoms of mercury may perhaps belong to the rosecobalt series, since it is formed by the addition of sodium-mercuric chloride to the soluble modification of rosecobaltic sulphate (see next page).

Antimonio-chloride.—The addition of a solution of antimonious chloride to one of purpureocobaltic chloride affords a precipitate of violet-red crystals, which are decomposed by water, with separation of SbOCl . The salt, after washing with strong hydrochloric acid, squeezing in blotting-paper, and drying at 100° , has the composition $\text{Co}^2(\text{NH}^3)^4\text{Cl}^4.\text{SbCl}^3$.

Bismuthous chloride gives, with solutions of purpureocobaltic chloride, a lilac-red precipitate, insoluble in hydrochloric acid and decomposed by water.

Neutral Chromate. $\text{Co}^2(\text{NH}^3)^4\text{O}^2.(\text{CrO}^4)^2$.—By mixing solutions of purpureocobaltic nitrate and neutral potassic chromate, a red crystalline precipitate is thrown down, which is soluble in hot water, soon decomposing, however, unless some free acid is present. Strong solutions of the salt are red; dilute solutions, orange-yellow. The equation representing its formation is—



The nitric acid thus liberated dissolves a portion of the salt, forming dichromate, which remains in solution.

When neutral potassic tungstate is digested with neutral purpureocobalt nitrate, a pink purpureocobaltic tungstate is formed, and the liquid then gives a strong acid reaction.

Neutral purpureocobaltic chromate yields, with potassium iodide, a red crystalline precipitate, for which no definite formula has yet been obtained, but it appears to be a mixture of the neutral chromate with iodochromate. The crystalline precipitate, formed by admixture of solutions of potassic chromate and purpureocobaltic chloride, is probably a mixture of the chromate and chlorochromate.

Dichromate. $\text{Co}^2(\text{NH}^3)^4(\text{Cr}^2\text{O}^7)^2.\text{H}^2\text{O}$.—A granular red precipitate, which may be crystallised from hot water—the crystals having then a brick-red colour with bronze

lustre—is obtained by mixing solutions of potassic dichromate and purpureo-cobaltic nitrate.

In preparing purpureo-cobaltic nitrate by the oxidation of ammoniacal cobalt nitrate with potassic dichromate (Mills' process), a large quantity of orange-red crystalline scales, with gold reflections, was obtained, which after recrystallisation, exhibited the composition $\text{Co}^2(\text{NH}^3)^{10}(\text{Cr}^2\text{O})^2 \cdot 5\text{H}^2\text{O}$.

With purpureo-cobaltic chloride, potassium dichromate gives a dark red crystalline precipitate, consisting of a mixture of chromate and chlorochromate of purpureo-cobalt.

Gibbs has also tabulated the formulæ of the less known compounds of the purpureo-, roseo-, and luteo-cobaltic series, as follows (*Deut. Chem. Ges. Ber.* ix. 187):

Purpureo-cobalt Series.

Basic Nitrate	$\text{Co}^2(\text{NH}^3)^{10}\text{O}(\text{NO}^3)^4 + 6\text{H}^2\text{O}$
Chloronitrate	$\text{Co}^2(\text{NH}^3)^{10}\text{Cl}^1(\text{NO}^3)^3 + \text{Co}^2(\text{NH}^3)^{10}(\text{NO}^3)^3$
Basic Tungstate	$\text{Co}^2(\text{NH}^3)^{10}\text{O}(\text{WO}^4)^2$
Chloroxalate (Krok)	$\text{Co}^2(\text{NH}^3)^{10}\text{Cl}^1(\text{C}^2\text{O}^4)^2$
Neutralised Sulphate	$\text{Co}^2(\text{NH}^3)^{10}(\text{SO}^4)^2 + \text{H}^2\text{O}$
Pyrophosphate (Braun)	$\text{Co}^2(\text{NH}^3)^{10}\text{P}^2\text{O}^{10} + 21\text{H}^2\text{O}$
Ammonio-cobalt Nitrite	$[\text{Co}^2(\text{NH}^3)^{10}][\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^3]^2$
Cobaltinitrate	$[\text{Co}^2(\text{NH}^3)^{10}(\text{NO}^2)^2][\text{Co}^2(\text{NO}^2)^{12}]^2 + 9\text{H}^2\text{O}$
Chlorofluosilicate	$\text{Co}^2(\text{NH}^3)^{10}(\text{SiF}^6)\text{Cl}^2 + 3\text{H}^2\text{O}$

Roseo-cobaltic Series.

Sulphates, α , β , γ	$\text{Co}^2(\text{NH}^3)^{10}(\text{SO}^4)^2 + 5\text{H}^2\text{O}$
Acid Sulphate	$\text{Co}^2(\text{NH}^3)^{10}(\text{SO}^4)^2 \cdot \text{SO}^4\text{H}^2 + 4\text{H}^2\text{O}$
Basic Oxalosulphate	$\text{Co}^2(\text{NH}^3)^{10}\text{O} \cdot \text{C}^2\text{O}^4 \cdot \text{SO}^4 + 7\text{H}^2\text{O}$
Acid Oxalodisulphate	$\text{Co}^2(\text{NH}^3)^{10} \cdot \text{C}^2\text{O}^4 \cdot (\text{SO}^4)^2 \cdot \text{C}^2\text{H}^2\text{O}^4 + 2\text{H}^2\text{O}$
Acid Oxalate	$\text{Co}^2(\text{NH}^3)^{10}(\text{C}^2\text{O}^4)^2 + 4\text{C}^2\text{H}^2\text{O}^4$
Mercurio-chloride	$\text{Co}^2(\text{NH}^3)^{10}\text{Cl}^1 \cdot 6\text{HgCl}^2 + 4\text{H}^2\text{O}$
Sulphatoplatino-chloride, β , γ	$\text{Co}^2(\text{NH}^3)^{10}(\text{SO}^4)^2\text{Cl}^2 \cdot \text{PtCl}^4$
Sulphatauro-chloride, β , γ	$\text{Co}^2(\text{NH}^3)^{10}(\text{SO}^4)^2\text{Cl}^2 \cdot \text{AuCl}^3 + 4\text{H}^2\text{O}$
Oxaloplatino-chloride	$\text{Co}^2(\text{NH}^3)^{10}(\text{C}^2\text{O}^4)^2\text{Cl}^2 \cdot \text{PtCl}^4$

Luteo-cobaltic Series.

Dichromate	$\text{Co}^2(\text{NH}^3)^{10}(\text{Cr}^2\text{O})^2 + 5\text{H}^2\text{O}$
Pyrophosphate	$\text{Co}^2(\text{NH}^3)^{10}\text{P}^2\text{O}^{10} + 6\text{H}^2\text{O}$
Cobaltionitrite	$\text{Co}^2(\text{NH}^3)^{12}[\text{Co}^2(\text{NO}^2)^{12}]$
Ammonio-cobaltionitrite	$\text{Co}^2(\text{NH}^3)^{12}[\text{Co}^2(\text{NH}^3)^4(\text{NO}^2)^3]^2$
Sulphatoplatino-chloride	$\text{Co}^2(\text{NH}^3)^{12}(\text{SO}^4)^2\text{Cl}^2 \cdot \text{PtCl}^4$

All these salts are crystallised. Gibbs has also obtained a new series of salts isomeric with the roseo-cobaltic salts, and having the yellow or orange-yellow of the luteo-salts. There are now, therefore, three series of roseo-cobaltic salts, represented by the ordinary sparingly soluble sulphate α , the soluble sulphate β , and the yellow sulphate γ .

The following ammonio-cobaltic compounds, in which the molecular ratio of ammonia to cobalt is $\text{NH}^3 : \text{Co}^2 = 8 : 1$, have been obtained by G. Vortmann (*Deut. Chem. Ges. Ber.* x. 154, 1451). They are prepared by the action of various acids on a solution of cobaltous carbonate in ammonia and ammonium carbonate oxidised by exposure to the air.

Octamine-purpureochloride, $\text{Co}^2(\text{NH}^3)^8(\text{H}^2\text{O})^2\text{Cl}^4$, crystallises in small octohedrons of a deep violet colour, easily soluble in water. It is isomeric with Rose's praseo-chloride, $\text{Co}^2(\text{NH}^3)^8\text{Cl}^4 \cdot 2\text{H}^2\text{O}$. These two salts readily admit of conversion, the one into the other.

Octamine-roseochloride, $\text{Co}^2(\text{NH}^3)^8(\text{H}^2\text{O})^2\text{Cl}^4 \cdot 2\text{H}^2\text{O}$, is obtained as a bright red precipitate.

Octamine sulphate, $\text{Co}^2(\text{NH}^3)^8(\text{SO}^4)^2 \cdot 6\text{H}^2\text{O}$, crystallises in needles having a bright red colour.

By adding alcohol to the aqueous solution of this salt, a second sulphate, $\text{Co}^2(\text{NH}^3)^8(\text{SO}^4)^2 \cdot 4\text{H}^2\text{O}$, is deposited in small needles of a red-violet colour.

Acid carbonate, $\text{Co}^2(\text{NH}^3)^8\text{O} \cdot (\text{CO}^2)^2 \cdot 2\text{H}^2\text{O}$, crystallises in long carmine-red prisms, soluble in water to a cherry-red solution.

Neutral carbonate, $\text{Co}^2(\text{NH}_4)^2(\text{CO}_3)^2 \cdot 3\text{H}_2\text{O}$, crystallises in small rhombic prisms of a pale violet colour, and forming a violet solution in water.

A sulphato-carbonate, $\text{Co}^2(\text{NH}_4)^2\text{SO}^4(\text{CO}_3)^2 + 3\text{H}_2\text{O}$, is obtained by precipitating a solution of cobaltous sulphate with an alkaline carbonate, dissolving the precipitate, which contains a considerable quantity of basic sulphate, in ammonia and ammonium carbonate, leaving the solution to oxidise in the air, and then treating it with alcohol. The double salt then separates in small copper-coloured plates.

See SULPHITES.

The poison of the Cobra de Capelle (*Naja tripudians*) which may be obtained by pressing the parotid glands of the snake while its fangs are erected, has been examined by A. Pedler (*Proc. Roy. Soc.* xxvii. 17) and by A. W. Blyth (*Analyst*, i. 204). It is an amber-coloured, syrupy, frothy liquid, of sp. gr. 1.048 (Blyth), 1.095 at 23° (Pedler). When evaporated, either in the air or in a vacuum, or at 100°, it leaves a solid residue amounting on the average to 28.82 per cent. (Pedler); about 33 per cent. (Blyth). The fresh liquid has no action on polarised light. It may be kept for two or three months without alteration, but after a year or eighteen months it alters considerably, becoming insoluble, and losing to a great extent its poisonous action (Pedler).

Dried in a vacuum over sulphuric acid, it gave by analysis:

C	H	N	Ash	O with trace of S
49.32	7.01	17.30	6.68	19.60 = 100.

or deducting the ash:

C	H	N	O and S
52.87	7.61	18.29	21.33 = 100.

This composition does not differ greatly from that of various kinds of albumin; the proportion of nitrogen, however, is rather greater than in egg-albumin.

The liquid poison, treated with strong alcohol, yielded a precipitate of albuminous matter, amounting to about 17.3 per cent. of the whole, which was only slightly poisonous, whereas the portion soluble in alcohol (10.9 per cent. of the whole) was excessively poisonous: hence, as the total quantity of solid matter in the poison is about 28 per cent., it follows that about 60 per cent. of the poisonous liquid is of an albuminous nature, and only about 40 per cent. consists of pure poison. No crystallisable substance could be obtained from the poison, either by the use of solvents, or by dialysis through parchment paper, although slight indications of crystallisation were obtained by both methods. The liquid remaining in the dialyser left on evaporation aummy mass, having all the physiological characters of the poison; and the liquid outside the dialyser appeared to be rather more poisonous than the original virus (Pedler).

According to Blyth, cobra poison contains albumin, a minute quantity of fat, and yields about 1.4-1.5 per cent. of ash mainly consisting of sodium chloride. It dries up quickly on exposure to the air, leaving a yellow acrid pungent powder, amounting to about 33 per cent. of the whole. This substance is not decomposed at 100°, but blackens at 270°, and yields a sublimate at higher temperatures. A similar substance crystallising in needles may be obtained by dialysing the poison. It exists therein to the amount of 10 per cent., and is highly poisonous, appearing to be the only active principle. It is obtained pure by conversion into a lead-salt, separation therefrom, and evaporation in a vacuum. Blyth designates this substance as *cobric acid*. He finds that a weak solution of potash, or a weak alkaline solution of potassium permanganate, destroys the physiological activity of cobra poison.

Pedler describes a long series of experiments on the modification of the active properties of the poison by various substances, undertaken with the view of discovering an antidote to its action. When the poison was digested with *ethyl iodide*, a residue was obtained which exhibited an increase of weight, indicating combination, and was much less active than the original poison. The residue obtained by mixing the poison with hydrochloric acid and leaving the liquid to evaporate, was also much less active than the original poison. By slow evaporation in a vacuum, distinct traces of crystals were obtained, but they were mixed with a large quantity of amorphous soluble matter, from which they could not be separated.

A much greater diminution of the activity of the poison is produced by the addition of *platinic chloride*. When a quantity of fresh cobra poison was treated with alcohol to precipitate the albumin, the alcoholic filtrate acidified with hydrochloric acid, and a solution of platinic chloride added, a small quantity of a yellow amorphous precipitate was formed, and the solution evaporated in a vacuum yielded a semicrystalline residue, which was freed from excess of platinic chloride by washing with weak spirit.

0.1 grm. of the solid platinum compound administered internally to a chicken exerted no poisonous action, and the solution containing the excess of platonic chloride was likewise without action when injected hypodermically. A considerable number of experiments upon chickens and dogs showed that even considerable quantities of cobra poison mixed with platonic chloride might be injected hypodermically without producing a fatal result, provided a short time was allowed to elapse before the mixture was injected. In one experiment, the quantity of poison thus injected was sufficient, if administered alone, to kill 120 chickens. When, on the other hand, the injection was performed immediately after mixing, the results were less favourable, the fatal effect being not prevented, but merely retarded. The same effect of retardation, but not prevention, of the fatal result, was obtained when the cobra poison was first injected alone, and the platinum solution a few minutes (1 to 5) afterwards. The poison appears indeed to diffuse itself through the organism so rapidly that no antidotes can be afterwards injected quickly enough to counteract its effects.

The platinum salt of the cobra poison gave by analysis numbers agreeing nearly with the formula $(C^{17}H^{23}N^4O^2.HCl)^2.PtCl^4$ (Pedler).

COCHLEARIA OIL. The essential oil of common scurvy-grass (*Cochlearia officinalis*) has the composition of a butylic thiocyanate (1st Suppl. 1056); and a comparison of its properties with those of the several isomeric compounds of this group, has shown that it is identical with the isothiocyanate or thiocarbimide obtained from secondary butyl alcohol—that is to say, with methyl-ethyl-thiocarbimide, $N \leq \overset{CS}{CH}(CH^3)(C^2H^3)$ (Hofmann, *Deut. Chem. Ges. Ber.* vii. 508).

COCOA-FAT, or CACAO-FAT. See THEOBROMA.

COCOA-NUT. The milk and fatty kernel of this seed (from *Cocos nucifera*) have been examined by F. Hammerbacher (*Landw. Versuchsstationen*, xviii. 472) with the following results:

The colourless, slightly opalescent fluid of the cocoa-nut, termed the milk, has a sp. gr. of 1.0442 at 20°. The total weight of liquid from two nuts amounted to 303.95 grams. It showed on analysis:

Water	91.50 per cent.
Protein	0.46 "
Fat	0.07 "
Non-nitrogenous extractive matter	6.78 "
Ash	1.19 "

The following are the results of the analysis of the ash of the milk and kernel:

	Ash of the milk	Ash of the kernel
Potash	55.200	43.882
Soda	0.728	8.392
Lime	3.679	4.628
Magnesia	6.606	9.438
Chlorine	10.373	18.419
Phosphoric acid	20.510	16.992
Sulphuric acid	5.235	5.091
Silicic acid	—	0.500
	<hr/> 102.331	<hr/> 102.342
Deducting oxygen replaceable by chlorine	2.338	3.024
	<hr/> 99.993	<hr/> 99.318

Hammerbacher also finds, in accordance with Lehmann, that the fat of the cocoa-nut consists in great part of free fatty acid.

CODINE. See OPIUM-BASES.

COLLESTIN. This mineral is found in the Keuper of Bristol. The ash of plants growing in the marl in which it occurs, contains strontium, whereas in plants growing on the neighbouring lias this element is absent (W. Stoddart, *Jahrb. f. Min.* 1876, 867).

CERULIGNONE, $C^{16}H^{16}O = C^{12}H^8 \left\{ \begin{smallmatrix} (OCH^3)^4 \\ (O-O) \end{smallmatrix} \right.$ (2nd Suppl. 376). The last products of the distillation of beech-tar oil yield, on further fractionation, a colourless liquid, which smells like creosote, boils at 270°, forms crystalline salts with ammonia and the fixed alkalis, and is converted by oxidising agents (potassium chromate, nitric acid, &c.) into cerulignone, $(C^{16}H^{16}O^2)$. At the same time there is formed another product of oxidation, which crystallises in large yellow needles, and dissolves in strong

sulphuric acid with a crimson colour, whereas cœrulignone forms a bright blue solution (A. W. Hofmann, *Deut. Chem. Ges. Ber.* 1874, 78).

Crude cœrulignone may be conveniently purified by suspending it in water and treating it with iron filings until its blue colour has completely disappeared, and only the brown tint of ferric hydrate is visible: the residue is then exhausted with alcohol, and the hydrocœrulignone crystallised after evaporation; finally, the alcoholic solution of hydrocœrulignone is treated with ferric chloride, whereby cœrulignone is thrown down in pure violet-red crystals, which are rendered blue by crystallisation from phenol (E. Fischer, *ibid.* 1875, 158).

Respecting the product formed by the action of sulphuric acid on cœrulignone, the observations of Fischer differ in some respects from those of Liebermann (2nd *Suppl.* 377). According to Fischer, this reaction yields a brown product sparingly soluble in cold water, more readily in hot water, ether, benzene, ligroin, &c.; readily soluble in alcohol, however, even when cold and somewhat dilute. It contains no sulphur, and is not converted into cœrulignone by oxidising agents such as ferric chloride or potassium dichromate. Reducing agents also (zinc and hydrochloric acid, or iron filings and acetic acid) have no action on it. Its solutions have a peculiar bitter taste; with alkalis it yields dark-green solutions, apparently forming saline combinations; the tinctorial power of these is great, and hence a very minute quantity of the compound can be readily detected by the addition of ammonia; acids reprecipitate the brown substance from solution. The body thus purified gives numbers agreeing with the formula $C^{12}H^{10}O^8$ (Liebermann obtained two compounds, viz. $C^{12}H^{10}O^8$ yellow, and $C^{12}H^{10}O^8$ orange-coloured), the potassium salt being $C^{12}H^{10}K^2O^8$ or $C^{12}H^{10}K^2O^8 \cdot 2H^2O$. The water of crystallisation is partly lost at 65° , wholly at 100° . This salt is precipitated by adding alcoholic potash to an alcoholic solution of the body, as it is less soluble in alcohol than in water. The barium salt, $C^{12}H^{10}Ba^2O^8$, can be obtained from this by double decomposition, or by adding an alcoholic solution of the substance very slowly to baryta-water; it is almost insoluble in water, quite insoluble in absolute alcohol and ether.

Use of Cœrulignone in Colour-printing.—To print silk or wool with cœrulignone hydrocœrulignone is dissolved in hot alcohol and precipitated by water, and the pasty precipitate is thickened with gum-water, printed on silk or wool, then dried and steamed. After steaming, the printed parts appear colourless, whilst before the steaming they appeared faintly coloured by the action of the air (cœrulignone being formed). When the thickening material is washed away, a bright orange tint is quickly developed on the printed parts by treatment in a bath of potassium dichromate or ferric chloride. The piece is then washed and finished. On cotton cœrulignone does not fix itself directly (B. Marx, *Dingl. pol. J.* cxxii. 355).

Substitution-products of Hydrocœrulignone (M. Hayduck, *Deut. Chem. Ges. Ber.* ix. 928-930). *Dichloracetylhydrocœrulignone*, $C^{12}H^8Cl^2(OCH^3)(OC^2H^3O)^2$, is obtained by trituration diacetylhydrocœrulignone with an equal weight of phosphorus pentachloride, and warming the mixture for a few minutes. It crystallises in small colourless prisms which melt at 172° .

Dichlorhydrocœrulignone, $C^{12}H^8Cl^2(OCH^3)(OH)^2$.—Diacetylhydrocœrulignone dissolves in alcoholic potash when boiled with it, but on continuing the boiling, the solution deposits an abundant precipitate, from the aqueous solution of which acids throw down a white gelatinous precipitate of dichlorhydrocœrulignone. This substance crystallises from hot alcohol in small, colourless, shining, rhombic tables, which melt at 220° . Its potassium-compound, $C^{12}H^8Cl^2(OCH^3)(OK)^2$, is nearly insoluble in alcohol, and is therefore precipitated in the foregoing reaction; it dissolves easily in water, and crystallises from strong solutions in needles. The barium-compound, $C^{12}H^8Cl^2(OCH^3)O^2Ba$, is thrown down as a white amorphous precipitate on adding barium chloride to a solution of the potassium-compound. It acquires a yellow colour when heated.

Dibromacetylhydrocœrulignone, $C^{12}H^8Br^2(OCH^3)(OC^2H^3O)^2$, is formed by adding to a solution of acetylhydrocœrulignone in glacial acetic acid the necessary quantity of bromine, precipitating with water, and crystallising the product from alcohol. It forms colourless needles melting at 178° .

Dibromhydrocœrulignone, $C^{12}H^8Br^2(OCH^3)(OH)^2$, is obtained by boiling the preceding compound with alcoholic potash, decomposing with hydrochloric acid the sparingly soluble potassium-compound thereby precipitated, and crystallising the product from boiling alcohol or benzene. It forms distinct prisms melting at 262° .

Tetrabromhydrocœrulignone, $C^{12}Br^4(OC^2H^3O)(OH)^2$, is formed in the same manner as the foregoing compound, an excess of bromine being employed. It crystallises in silky needles melting at 217° - 218° .

COFFEE. The composition of various kinds of coffee has been determined by O. Levesie (*Arch. Pharm.* [3], viii. 294) with the following results:

	Gummy matter	Caffeine	Fat	Tannic and caffe-tannic acid	Cellulose	Ash	Potash	Phosphoric acid
Finest Jamaica plantation	25.3	1.43	14.76	22.7	33.8	3.8	1.87	0.31
Finest green Mocha	22.6	0.64	21.79	23.1	29.9	4.1	2.13	0.42
Ceylon plantation	23.8	1.53	14.87	20.9	36.0	4.0	—	0.27
Washed Rio	27.4	1.14	15.95	20.9	32.5	4.5	—	0.51
Costa Rica	20.6	1.18	21.12	21.1	33.0	4.9	—	0.46
Malabar	25.8	0.88	18.80	20.7	31.9	4.3	—	0.60
East Indian	24.4	1.01	17.00	19.5	36.4	—	—	—

The quantities of glucose and caffeine in several kinds of coffee have also been determined by C. H. Eddy (*American Chemist*, vii. 45):

	Glucose and Caffeine
Slightly roasted Maracahibo	3.805 per cent.
Well-roasted Mocha	2.118 "
Well-roasted Java	1.991 "

Commalleo (*Moniteur scient.* [3], vi. 779) has also investigated the composition of coffee. The following table exhibits his results, in comparison with the older determinations by Payen and by von Bibra (i. 1070):

	Commalleo. Undressed Mysore coffee	Payen	
Hygroscopic Water	from 6.3 to 15.7 *	10	p.c.
Fatty matters	12.68	10-13	"
Glucose	2.60	—	"
Dextrin	—	15.5	"
Legumin. Casein	1.52	10	"
Albumen	1.04	—	"
Potassium-caffeine Chloride	—	3.5-5	"
Free Caffeine	—	0.8	"
Total quantity of Caffeine †	from 0.42 to 1.31	1.815-2.50 †	"
Ash	3.882	6.697	"
Coffee extract with cold water	24.97	—	"
" " warm water	37.20	—	"
" " alcohol of 60 p.c.	23.15	—	"

On the Estimation of Caffeine in Coffee, see **CAFFEINE** (p. 370).

Detection and Estimation of Chicory, &c.—To detect chicory in coffee, Wittstein (*Dingl. pol. J.* ccxv. 84) dilutes the decoction with eight times its bulk of water, filters, and increases the dilution to 12 parts. If the decoction contains pure coffee, on adding to 30 drops of it 2 drops of concentrated hydrochloric acid, boiling for a few seconds, then adding 15 drops of a solution of 1 part of potassium ferrocyanide in eight parts of water, and boiling as before, the solution becomes first green, then dark green. Six drops of potash are next added, and the whole is boiled for two minutes, the solution becoming first brown and finally clear pale yellow, with a slight dirty yellow precipitate. With chicory alone, the solution finally remains brown and turbid, and after long standing a precipitate falls, the supernatant liquid retaining its brown colour. With a mixture of 24 drops of coffee and 6 of the chicory decoction, a brown turbid solution is finally obtained. A decoction of coffee of average strength contains 1 per cent., and of great strength barely 2 per cent. of the dry soluble matter. The evaporation-residue consists of a deep brown, shining, varnish-like mass, feeling quite dry to the touch after two days. If the ordinary substitutes for coffee are present, this residue becomes sticky after standing for an hour or two, and quite damp in twenty-four hours.

* These two numbers give the highest and lowest results of 24 determinations.

† In the proportion of 29 caffeine to 100 salt (according to Payen).

‡ These numbers give the proportion 0.8 free caffeine to 1.015-1.450 combined caffeine. The last number, 2.50, for the total amount is probably too high, as it has not yet been found possible to extract from coffee more than 2 per cent. of caffeine.

A. H. Allen (*Chem. News*, xxix, 123, 129) recommends that a preliminary examination be made by strewing the powder over the surface of cold water; coffee then floats, whereas chicory, caramel, &c., quickly sink. On stirring, coffee colours the liquid but very slightly, whereas chicory, &c. colour it dark brown.

The amount of ash in genuine coffee does not exceed 4.5 per cent.; chicory yields 5 per cent. The silica in coffee-ash never exceeds 1 per cent., while in chicory it varies from 10–36 per cent. The average soluble ash in coffee is 3.24, while in chicory it is only 1.74 per cent. By determining the soluble ash, S, the percentage of pure coffee, C, may be calculated by the formula: $C = \frac{2(100S - 174)}{3}$.

The density of coffee-infusion is determined by heating the powder with 10 times its weight of cold water, raising the liquid to the boiling point, filtering, and taking the density at 15.5°. Taking the density of pure coffee-infusion at 1008.6, and that of chicory at 1020.6, the percentage of pure coffee, C, in a sample may be calculated from the equation $C = \frac{100(1020.6 - D)}{12}$, where D represents the density of the infused sample.

The relative tinctorial power of an infusion of a sample of coffee is determined by boiling a given weight with 20 c.c. of water for a few minutes, filtering, and again boiling the residue until thoroughly exhausted. An equal weight of a standard mixture of equal parts of pure coffee and chicory is treated in a precisely similar manner. The standard solution is made up to 200 c.c., that of the sample to 100 c.c.; 10 c.c. of the latter are put into a narrow burette, and some of the standard into a test-tube of exactly equal bore. If the tints are exactly the same, the sample consists of pure coffee; if chicory is present, water must be added to the sample until the tints are the same. Each c.c. of water corresponds with 5 per cent. of chicory.

The presence of leguminous seeds or cereals may be detected by boiling the sample with animal charcoal and water, filtering, and testing for starch in the cold liquid with iodine. Neither coffee nor chicory contains starch.

According to E. Dannenberg (*Arch. Pharm.* [3], x, 97) it is best, in applying the Sims-Otto process for the detection of alkaloids, to use chloroform or amyl alcohol, instead of ether, for separating colchicine, as these reagents are more energetic in their action, and capable of dealing with smaller quantities of the alkaloid. The best test for colchicine is *nitric acid*, which gives a clear rose colour when all other tests fail.

Flückiger (*Pharm. J. Trans.* [3], vii, 372) recommends a solution of colchicine diluted till it becomes colourless, as a test for *mineral acids*. Strong sulphuric or nitric acid colours this solution yellow; and a drop of hydrochloric acid colours it bluish-violet. If a solution of colchicine to which a drop of nitric acid has been added be strongly concentrated, and a trace of sodium acetate then added, the liquid will assume an orange colour. On mixing a solution of colchicine with sulphuric acid, and adding a small quantity of a mixture of 50 pts. potassium iodide and 13.5 mercuric iodide, a precipitate is formed. This method will detect $\frac{1}{2}$ per cent. sulphuric acid in vinegar.

Alkaloid in Beer resembling Colchicine.—This alkaloid, found by Dannenberg (*Arch. Pharm.* [3], viii, 411) in a sample of beer of unknown origin, is amorphous, bitter, soluble in water and in alcohol, and is separated from its acid aqueous solution by chloroform and by ether, less easily, however, by the latter. Its reactions with the ordinary tests for alkaloids exactly resemble those of colchicine (i. 1081), excepting that nitric acid of sp. gr. 1.48 dissolves it with a fine reddish-violet colour, and that a mixture of nitric and sulphuric acids colours it rose-red. The red-violet coloration with nitric acid has, however, been also observed by Dannenberg in cases when colchicine was known to be present, whence he is inclined to believe that the beer alkaloid is identical with colchicine.

According to H. van Geldern, on the other hand (*Arch. Pharm.* [3], ix, 32), the body resembling colchicine is neither identical with the latter, nor indeed an alkaloid at all; it originates from hops, and gives the reactions of an alkaloid with potassium iodide and tannin only when gelatin is present. Its reaction with nitric acid varies, sometimes giving a splendid reddish-violet colour, sometimes a dingy red. A mixture of unadulterated hops and gelatin was found to exhibit all the reactions of colchicine, that of nitric acid, however, being indistinct.

■, $C^{10}H^{10}O^3$ (Church, *Chem. Soc. Jour.* 1877, i, 253). A red colouring matter contained in the stems and leaves of *Coleus Verachaffeltii*, from which it may be obtained by extraction with alcohol slightly acidulated with sulphuric acid, the acid being then removed by barium carbonate, and the alcohol by distillation. *Eos*

purification, the residue is dissolved in alcohol; the colouring matter is precipitated from the solution by ether; the precipitate redissolved in alcohol; the solution poured into water; and the resulting precipitate repeatedly washed with water at 50°–60°. Colein thus purified gives, by analysis numbers agreeing with the formula $C^{10}H^{10}O$. Its alcoholic solution, treated with excess of lead-acetate, yields a precipitate of a dark indigo-coloured lead salt having the composition $C^{20}H^{10}PbO^{10}$.

Colein when pure is a brittle solid, having a resinous aspect and conchoidal fracture, and yielding a reddish-purple powder. It is insoluble in ether, and only slightly soluble in water, but dissolves easily in alcohol, forming a crimson solution, which gradually becomes colourless, in consequence of the formation of a compound of the colouring matter with the alcohol. On evaporating the solution, or adding an acid, the crimson colour reappears. On gradually adding ammonia to a solution of colein, the colour changes successively to purple-red, violet, indigo, chrome-green, and finally to yellow-green. Stannic chloride, added to the concentrated alcoholic solution, forms a precipitate of a fine violet colour. With strong sulphuric acid colein forms an orange-coloured solution, which, on dilution with water, exhibits the red colour and other characters of an acid solution of unaltered colein. Sulphuric acid of sp. gr. 1.53 dissolves colein with crimson colour. Nitric acid converts colein into a brown resinous mass.

COLLIDINE, $C^8H^{11}N$. Krämer obtained this base by the action of ammonia on ethylidene chloride, $CH^3.CHCl^2$ (2nd Suppl. 378); and Tawildarow has shown that it is formed in like manner from ethylidene bromide, most readily at 125°–140° (*Liebig's Annalen*, cxxvi. 12).

COLOPHENE, $C^{20}H^{12}$. Diterobene. See TEREBENE.

COLOPHONY. This resin distilled with lime in an iron retort, gives off gases of the series C^8H^{12+2} , also propylene, amylene, acetone, and a body having the composition $C^8H^{10}O$ (Bruylants, *Deut. Chem. Ges. Ber.* viii. 1463).

When colophony is distilled with overheated steam at a comparatively low temperature, benzene is produced in somewhat considerable quantity, and at a higher temperature, toluene (Watson Smith, *Chem. Soc. J.* 1876, ii. 29).

Colophony is readily oxidised by boiling it in a retort with a mixture of 1 pt. strong commercial nitric acid and 2 pts. water, the products consisting chiefly of isophthalic and trimellitic acids. The syrupy mother-liquor, further treated with fuming nitric acid, yielded an indistinctly crystalline mass consisting chiefly of terobic acid (Schreder, *Liebig's Annalen*, cxxii. 93).

COLUMBITE. See NIOBATES.

COLUTEA. The gas enclosed in the fruit of the Bladder Senna (*Colutea arboreasens*) is not common air, but a mixture containing a smaller proportion of oxygen, and 0.50 to 2.32 per cent. of carbon dioxide. These fruits, though green absorb oxygen, and give out carbon dioxide by night as well as by day; and the amount of carbon dioxide produced is greater than that which the oxygen absorbed would furnish. In this plant there are, therefore, green organs which act like the animal tissues and the coloured parts of other vegetables (Saint Pierre a. Magnien, *Compt. rend.* lxxxiii. 490).

COMBUSTION. *Influence of Pressure*.—Candles, sulphur, potassium, and carbon disulphide, burning under pressures of 30 and 35 atmospheres, give out a brighter light than when they burn in the open air. The flame of phosphorus exhibits no such increase of luminosity under increased pressure. With the first mentioned substances, the chemical activity of the rays, as shown by their action on phosphorescent bodies, likewise becomes greater under increased pressure (Caillaet, *Compt. rend.* lxxx. 487; *Ann. Chim. Phys.* [5], vi. 429).

Wartha (*J. pr. Chem.* [2], xiv. 81) finds that stearin candles, which in the open air burn with a flame 4.5 to 6 c.m. long, produce, under a pressure of 1.96 atmospheres, a very smoky flame from 9 to 10 or even 12 c.m. long. Under the increased pressure, the flame also becomes yellowish-red and less luminous. A candle, which when burning in the open air, lost 9.34–10.7 grams per hour, lost under 1.95 atmospheres from 7.86 to 9.22 grams per hour. The rate, therefore, the medium in which the candle burns, the greater is the hourly loss of combustible matter. Under the receiver of an air-pump, the brightness of the flame began to diminish with the exhaustion, the flame at the same time swelling out, and the inner blue cone separating itself completely from the wick. From time to time a shower of fine sparks was thrown out from the interior of the flame, most abundantly at the stage of greatest rarefaction (30 mm.) Within certain limits, therefore, the combustion is more complete as the medium is more rarefied (*comp. Frankland*, i. 1100; ii. 654).

Combustion of Detonating Gaseous Mixtures.—According to Neyreneuf (*Compt. rend.* lxxx. 118, 335, 685), when detonating gaseous mixtures are burnt in cylindrical tubes, in such a manner that the combustion of the first portions can communicate to the successive layers a regular vibratory motion, the flame will warm certain parts of the tube for a longer time than the rest. When the detonating mixture consists of hydrogen and oxygen, the water-vapour formed condenses chiefly on the parts of the tube which are left cool, and in such a manner as to show that, in spite of the violent shock produced by the detonation, the flame travels along the tube in waves.

On the Temperature at which Combustion begins, see A. Mitscherlich (*Deut. Chem. Ges. Ber.* ix. 1171); Berthelot, (*Compt. rend.* lxxiv. 407); also *Chem. Soc. J.* 1877, i. 42, 680).

On the Imperfect Combustion of Gases and Gaseous Mixtures, see the article **CHEMICAL ACTION** in this volume, pp. 430-436; also **FLAME**.

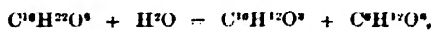
FE. This variety of thomsonite (v. 785) is found, together with phillipsite and chabasite, in drusy cavities of the leucito-nephelin basalt to the south-west of Waltzsch in Bohemia. The comptonite occurs in small, nearly colourless crystals, exhibiting the usual combination $\alpha P\infty : \alpha P\infty : \alpha P$, with a very obtuse macrodome of $177^{\circ} 35'$. It forms thin yellowish- and greyish-white druses, covered here and there with a very soft, thin, botryoidal crust of stilpnomerite, mostly converted into limonite, on which are implanted small isolated crystals of phillipsite. These latter form intersecting twins, with coincident principal axes, of the combination $\alpha P\infty : \alpha P\infty : P$. Some of the drusy cavities of the basalt are lined with very small crystals of chabasite, mostly intersecting twins of R. In the midst of them was found a single crystal of phillipsite covered with very small crystals of chabasite. The order of succession is therefore: comptonite, phillipsite, chabasite (Boricky, *Jahrbuch für Mineralogie*, 1873, p. 162).

CONCHININE. See **CINCHONA BARKS** (p. 492).

CONIFERIN. The alcoholic solution of this glucoside (obtained from the cambium of coniferous woods; *1st Suppl.* 489) may be advantageously decolorised either by the addition of lead acetate and ammonia, or by heating with animal charcoal. The crystals of coniferin contain $C^{10}H^{22}O^8 + 2H^2O$, lose part of their water on exposure to the air, and the whole at 100° . With concentrated sulphuric acid coniferin strikes a violet colour which soon becomes red, similar tints being produced by the addition of a large proportion of sulphuric acid to its aqueous solution. On diluting the sulphuric acid solution, a blue resin is deposited, and coniferin, when moistened with phenol and sulphuric acid, acquires a deep blue colour, this reaction being facilitated by exposure to sunlight; the well-defined reaction of pipe-wood with phenol and sulphuric acid is no doubt due to the presence of coniferin. Coniferin does not reduce Fehling's solution even at the boiling heat; but strong acids or hot dilute acids convert it into glucose and a resinous product (Tiemann a. Haarmann).

CONIFERYL ALCOHOL or **CONIFEROL**, $C^{10}H^{12}O^8 \sim C^9H^{11} \begin{matrix} OCH^2 \\ | \\ OH \\ | \\ C^9H^9OH \end{matrix}$

(Tiemann a. Haarmann, *Deut. Chem. Ges. Ber.* vii. 608). This compound, isomeric with ethyl-vanillin (from potassium-vanillin and ethyl-iodide, p. 305), is produced, together with glucose, by digesting coniferin with water and a small quantity of emulsin:



The best way of preparing it is to drench 50 grams of pure coniferin with 500 grams of water, add 0.2-0.3 gram of dry emulsin, and leave the whole to itself at a temperature of 25° - 36° for six or eight days, by which time the fermentation will be completed, the coniferin will have disappeared, and in its place will be found a flocculent crystalline body, while glucose remains in solution. By repeatedly agitating the whole with ether, and distilling off the latter, the coniferol will be obtained in the form of a quickly solidifying oil; or by not pushing the evaporation of the ether quite so far, it may be obtained directly in the form of white prismatic crystals.

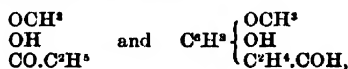
Coniferol melts at 73° - 74° (ethyl-vanillin at 64° - 65°), dissolves easily in ether, less easily in alcohol, sparingly in hot water, and is almost insoluble in cold water. It dissolves in alkalis, but is precipitated therefrom by acids, not in the crystalline, but in the amorphous state, in which it is less soluble in alcohol and ether, and forms, when dried at 100° , a white powder easily turning yellow or yellowish-red, and softening at 160° - 160° after the manner of resins. A substance of similar properties is precipitated on adding a few drops of sulphuric or hydrochloric acid to a solution of crystallised coniferol in water or dilute alcohol; and identical with it is also the resin produced by the action of acids on coniferin. The amorphous substance has the

same composition as crystallised coniferol, and is probably a polymeric modification thereof. Both are coloured red by strong sulphuric acid, and afterwards dissolved with red colour.

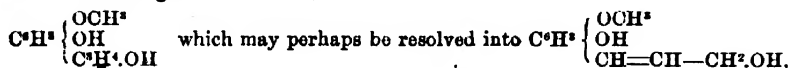
Crystalline coniferol when exposed to the air acquires the odour of vanilla, and the same odour is produced when either coniferol or coniferin is oxidised by chromic acid mixture. On distilling the product, aldehyde first passes over, then a distillate which smells like vanilla; and from this distillate ether extracts the odorous principle. The latter is, however, best obtained by oxidising coniferol, and agitating the product directly with ether, which, when evaporated, leaves the odorous principle as an oil which solidifies on cooling. The substance thus obtained is identical in every respect with vanillin from vanilla.

Coniferol was at first regarded by Tiemann & Haarmann as identical with ethyl-vanillin; but the two bodies differ in melting point by nine degrees, and likewise in their behaviour with bases. Coniferol, indeed, forms salts like a phenol, and must therefore be supposed to contain phenolic hydroxyl, as represented by the formula $C^6H^4(OCH^3)(OH)(C^6H^4OH)$. The potassium and sodium salts may be obtained in crystalline forms by leaving solutions of the alcohol in dilute potash or soda to evaporate slowly at ordinary temperatures and under reduced pressure. On treating the alcohol, while still in the oily state, with strong ammonia, the ammonium salt is formed, and immediately solidifies to a radio-crystalline mass; the aqueous solution of this salt when left in an open vessel, gives off ammonia, and yields coniferol in fine crystals. From a solution of coniferol in dilute alcohol, a lead salt is precipitated by lead acetate and ammonia, in white amorphous flocks.

The phenolic nature of coniferol is further shown by its reaction with nitric acid, whereby, according to the conditions of the experiment, it is either wholly destroyed or converted into picric acid; also, by its behaviour to oxidising agents, which attack it but slowly. The two other possible formulæ,



must be rejected,—the first, because a compound thus constituted would yield by oxidation, not vanillin, $C^6H^4O^3$, but vanillic acid, $C^6H^4O^4$; the second, because it represents an aldehyde, and coniferol does not exhibit the properties of that class of bodies. According to the formula,



coniferol should be nearly related to eugenol, $C^6H^3(OCH^3)(OH)(C^6H^4)$, which, indeed, appears to be formed from it by fusion with potash, or by heating with water and sodium-amalgam (Tiemann, *Deut. Chem. Ges. Ber.* viii. 1127).

CONIMA or INCENSE RESIN (Stenhouse and Groves, *Chem. Soc. J.* 1876, i. 175). This resin, also called 'Gum Hyawa,' is the produce of the 'Hyawa' or Incense tree (*Iceia heptaphylla*, Aubl.), indigenous in British Guiana, and has a pleasant balsamic odour, due to an essential oil, which, however, is present in small quantity only. The resin contains but a very small proportion of extraneous matters insoluble in spirit, but it is very unequal in appearance, some portions being of a pale yellow colour, and soft enough to be moulded between the fingers, whilst others are white and crystalline.

Conimene, C^6H^4 .—To obtain the essential oil, the resin was distilled in the usual way with a large quantity of water (a current of steam might also be employed); and the oil, which came over with the aqueous vapour and separated as a thin layer floating on the surface of the water in the receiver, was collected and put aside. After standing for some time until the suspended water had sunk to the bottom of the vessel, the pale yellow oil was subjected to fractional distillation. The greater portion came over between 260° and 275° , the fraction boiling above that temperature having a bluish-green colour by transmitted light. In order to purify the hydrocarbon from any oxygenated compounds it might contain, the whole of that which came over below 275° was digested for several hours with clean metallic sodium; this caused the formation of a brown flocculent substance. The oil was then poured off from the unattacked metal, distilled, and again digested with sodium, these operations being repeated five or six times. The oil was then submitted to a careful fractional distillation, when it began to boil at 150° , but the temperature rose rapidly until it had reached 265° ; the fraction boiling at 255° – 270° was then repeatedly rectified off sodium, when ultimately about half of it was obtained in the pure state, boiling con-

stantly at 264°. Before treatment with sodium, the constant boiling point appeared to be near 270°.

The oil thus purified gave by analysis 88.00 to 88.24 per cent. carbon, and 11.63 to 11.66 hydrogen, the formula $C^{12}H^{10}$ requiring 88.24 C. and 11.76 H, the slight deficiency, 0.3 per cent., being no doubt due to the presence of a small quantity of an oxygenated oil. This result, viewed in connection with the boiling point, shows that conimene, in common with many other hydrocarbons obtained from similar sources, must be regarded as belonging to the group of sesquiterpenes, $C^{12}H^{14}$.

Conimene is a colourless, mobile liquid, which, like the other members of the group, is nearly insoluble in water, but readily miscible with alcohol, ether, and benzene. It has a pleasant aromatic odour, and burns with a smoky flame. Concentrated sulphuric acid acts strongly on it, much heat being developed when the two are mixed; this is apparently due to the polymerising effect of the acid. The product has the same odour as the corresponding compound formed by the action of the acid on turpentine.

Crystalline Resin of Conima. *Icacine*, $C^{16}H^{16}O$.—The natural resin contains, besides the hydrocarbon, a crystalline compound and an amorphous resin. In order to obtain these, the solid residue in the retort remaining after the essential oil had been removed by distillation in a current of steam, was dried as far as possible, and digested with six times its weight of strong spirit. It dissolved almost entirely, and on cooling deposited a mass of silky needles of the crystalline compound, mixed with the insoluble extraneous matter originally present in the resin. The product, after being separated from the mother liquors and washed slightly with cold spirit, was dried and dissolved in thirty times its weight of that solvent. The hot filtered liquid, on cooling, formed a semi-solid pulpy mass of colourless crystals of the nearly pure substance, amounting to about 20 per cent. of the weight of the original resin.

The yellow amorphous resin, which is very soluble in spirit, may be obtained from the original mother-liquors on evaporation; but it exhibits no points of special interest.

The crystals, although apparently pure, still retain a small amount of a brown amorphous substance, which may be removed by dissolving them in petroleum boiling below 35° (25 pts.) The hot-filtered solution, on standing, slowly deposits the substance in tufts of needles of dazzling whiteness. These, after being again crystallised once or twice from spirit to remove traces of petroleum, are quite pure. They then melt at 175°; but if the subsequent crystallisation from spirit has been omitted, they will be found to melt at 165°–168°, as the presence of even a very minute quantity of petroleum lowers the fusion point considerably.

Icacine dried at 100° gave by analysis 85.51–85.71 per cent. carbon, and 11.64 to 11.94 hydrogen, the formula $C^{14}H^{14}O$, requiring 85.71 C., 11.80 H., and 2.49 O. It does not appear to possess acid properties, as it is insoluble in aqueous alkalis, and alcoholic potash does not exert a perceptibly greater solvent action on it than alcohol itself.

The crystals are insoluble in water, only moderately soluble in boiling alcohol or petroleum, but readily soluble in ether, carbon bisulphide, and hot benzene. They are attacked with violence by concentrated nitric acid, and dissolve readily in about twelve times their weight of the acid, with abundant evolution of nitrous fumes. On pouring the product into water after these fumes cease to be given off, a pale yellow flocculent precipitate is formed, which slowly agglutinates to a resinous mass, not yielding any crystalline substance. On evaporating at a gentle heat the clear aqueous solution from which the resin had separated, a pale yellow mass of the consistence of honey was obtained, which showed no signs of crystallisation, even after being put aside for some months.

Icacine dissolves in warm concentrated sulphuric acid with a pale brown colour, and when more strongly heated becomes black, and evolves sulphurous anhydride.

The natural resin has been employed as a substitute for incense, either alone or mixed with other odiferous gums, and may also be useful for pastiles. Its usefulness in this respect is entirely due to the essential oil which it contains, as neither the crystalline nor the amorphous resin, when heated alone, gives an odour at all resembling that of incense.

CONINE, $C^8H^{11}N$. According to Grunzweig (*Liebig's Annalen*, cxlii. 193), natural conine oxidised with chromic acid yields normal butyric acid. It is therefore a normal butyl derivative, and the differences observed between natural and artificial conine (1st Suppl. 381) must be due to circumstances independent of any differences in the carbon groups which they contain.

Hydrobromide.—Conine, neutralised with hydrobromic acid, forms a hydrobro-

vide which crystallises in colourless prismatic needles, dissolves very easily in water and in alcohol, sparingly in ether and in chloroform. It is scentless and nearly tasteless; turns red when exposed to light, but remains unaltered in the dark; smells like conine when rubbed between the fingers; melts at about 100°. The conine used for preparing this salt should be as white as possible; otherwise, the purification will be attended with great loss (Mourrut, *Pharm. J. Trans.* [3], vii. 23).

Periodide.—When an alcoholic solution of conine is mixed by drops with an alcoholic solution of iodine, then left to evaporate, the residue taken up with water, and the solution left over calcium chloride, the compound $C^8H^{14}N.H.II^2$ is obtained in large octohedrons, easily soluble in water, alcohol, ether, and chloroform; insoluble in benzene, nearly insoluble in carbon sulphide, and decomposed easily but not completely, by silver nitrate (H. R. Bauer, *Arch. Pharm.* [3], v. 214).

Hydro-sulphide.—An alcoholic solution of conine treated with hydrogen sulphide yields crystals of an unstable compound, apparently having the composition $C^8H^{14}N.H^2S$ (Schmidt, *Deut. Chem. Ges. Ber.* vii. 1525).

Reaction with Aldehydes.—This reaction takes place according to the equation



but the purification of the products is much impeded by the condensation of the aldehydes which takes place at the same time. The aldehydic derivatives of conine have little or no basic character (H. Schiff, *Deut. Chem. Ges. Ber.* vi. 143).

COPAIBA. According to Wayne (*Amer. Journ. of Pharmacy* [4], iii. 326), the best test for the adulteration of copaiba balsam with castor oil is petroleum-ether, which completely dissolves the pure balsam, but leaves the castor oil undissolved. According to Muter (*Analyst*, i. 160), the solubility of the sodium salts of the acids of copaiba balsam in a mixture of 5 pts. ether and 1 pt. alcohol, may be made available for the detection of fixed oils in the balsam.

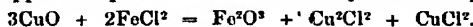
According to Siebold (*Pharm. J. Trans.* [3], viii. 250), the best method of testing the purity of copaiba is to evaporate 1 to 1.5 gram of the sample until all the oil is expelled. In the absence of fatty oil, the resin will be brittle and pulverisable, but 1 per cent. of fatty oil diminishes the brittleness, and with 3 to 5 per cent., the resin feels sticky. Castor and linseed oils may be distinguished by their odours when the resin is heated. Small quantities of oil of turpentine can be detected by taking the boiling point of the sample, oil of copaiba boiling at 240°–250°, and oil of turpentine at 160°. If the oil of turpentine present amounts to 2½ per cent. of the balsam, it will distil over before the copaiba oil.

See also Bowman (*Pharm. J. Trans.* [3], viii. 330; *Chem. Soc. J.* 1877, ii. 932).

COPPER. *Extraction.*—T. S. Hunt and J. Douglas (*American Chemist*, 1870, p. 198) have devised a process for obtaining copper from its ores, founded on the following reactions established by the experiments of Hunt. Cuprous chloride dissolves not only in solutions of the chlorides of alkali-metals and alkaline-earth metals, but likewise in zinc chloride, manganoous chloride, ferrous chloride, cupric chloride, &c., producing loosely combined double salts, from which the cuprous chloride is precipitated on dilution with water. These double salts are likewise produced by the action of the oxides of copper on ferrous chloride in presence of sodium chloride. Cuprous oxide dissolves in a solution of ferrous chloride, with precipitation of a mixture of ferric oxide and copper:



Cupric oxide likewise precipitates ferric oxide from a solution of ferrous chloride, but the whole of the copper then passes into solution as cuprous and cupric chloride:



This reaction is complete and takes place quickly, especially in presence of common salt, and under the influence of heat. When an excess of cupric oxide is used, insoluble oxychlorides are produced; the ferric oxide precipitated in the preceding reactions likewise always contains small quantities of chloride.

The extraction of the ores is performed in a bath containing ferrous chloride, produced by the mutual action of ferrous sulphate and a chloride: 120 lbs. of common salt or 112 lbs. of calcium chloride, and 280 lbs. of ferrous sulphate are dissolved in 100 gallons of water, and 200 lbs. of common salt are added to the liquid. These quantities are sufficient for the chlorination and solution of 90 lbs. of copper. From this solution the copper is precipitated by scrap iron, which at the same time restores the bath to its original state, so that only an eighth part of fresh lye requires to be added for each successive operation. Ores which contain the copper as oxide can be treated immediately by this process; carbonates require previous ignition; pyritic ores must

be roasted. The advantage of the process depends on the fact that the greater part of the copper exists in the solution as cuprous chloride, which may of course be precipitated by a quantity of iron smaller than that which is required for the decomposition of the cupric chloride present in the solutions obtained by the methods of extraction hitherto adopted.

According to a report by F. Wimmer (*Chem. Centr.* 1873, 104), this process is profitably worked in Chile and North Carolina.

According to R. Siemens, on the other hand (*Dingl. pol. J.* cccx. 184), it can be advantageously applied only to rich copper ores. Poor ores, which do not admit of elaborate preparation, soon become covered with a crust of ferric oxide, which absorbs the carbonic acid gas evolved from the copper carbonates, and then becomes impervious to the liquid. To prevent this incrustation of the ores with ferric oxide, they must be reduced to fine powder, and roasted at a temperature high enough to expel carbon dioxide from the copper carbonates, but not to decompose calcium carbonate. Continual stirring and warming of the solution are also necessary to ensure the dissolution of the cuprous chloride, and subsequent washing of the ores with hot water is likewise indispensable. All these operations are too costly to be profitably applied to any but rich ores, which, on the other hand, can be more advantageously worked by smelting. Poor ores can be more economically lixiviated with hydrochloric acid.

Treatment of Sulphuretted Copper Ores.—1. Monnier's method consists in roasting the ore with sodium carbonate, whereby acid sodium sulphate is formed, together with iron and copper sulphates. On raising the temperature, the free acid of the sodium salt acts upon the still unroasted metallic sulphides. The heat is increased till the iron sulphate is decomposed, after which the copper sulphate is dissolved out by water, and the solution evaporated to the crystallising point, whereupon about four-fifths of the cupric sulphate crystallises out. The mother-liquor is evaporated to dryness; the residue ignited; the sodium-salt removed by washing; and the cupric oxide which remains is smelted to obtain the metal.

2. The following method is adopted at the Bede Metal Works, Jarrow, for extracting copper from the residues obtained in burning pyrites for the manufacture of sulphuric acid. These residues always contain a quantity of sulphur sufficient to hold in combination the 2-4 per cent. of copper present in them. They are first roasted with addition of common salt, so as to convert the copper completely into sulphate, which then reacts with the sodium chloride, forming sodium sulphate and cupric chloride. Mr. Gibb, the Director of the above-mentioned works, has constructed a mechanical roasting furnace, by means of which the roasting may be completely effected with so small a quantity of common salt, that the resulting sodium sulphate is pure enough to be used for the manufacture of soda. The roasted masses are lixiviated with water and hydrochloric acid (condensed from the gases evolved from the roasting furnaces), and the copper is precipitated from the solution by hydrogen sulphide. The liquid filtered from the copper sulphide is evaporated to dryness; the residue, after calcination, is ignited with charcoal; the melted mass containing sodium sulphide, formed by reduction of the sulphate, is dissolved in water; and carbonic acid gas is passed into the solution, whereby sodium carbonate is formed, with evolution of hydrogen sulphide. The soda-solution is evaporated to dryness, and the hydrogen sulphide is utilised for precipitating copper (*G. Lange, Dingl. pol. J.* cci. 288).

On the Treatment of poor Copper Ores, see also *Dingl. pol. J.* cccx. 349; ccxvii. 478; *Chem. Soc. J.* 1874, 1117; 1876, i. 795.

Use of Phosphorus in the Refining of Copper.—The addition of phosphorus in that part of the operation of refining copper known as 'poling,' increases the density of the refined metal, and at the same time assists the deoxidation, thereby accelerating the process, and dispensing to a considerable extent with the use of the pole. It does not, however, appear desirable to effect the deoxidation entirely by phosphorus, but rather to bring the metal by its agency near to the tough-pitch point, and then complete the process by the less rapid action of the pole. The phosphorus is added in the form of a phosphide of copper containing about 7 per cent. of phosphorus, prepared by pouring melted copper upon sticks of phosphorus placed at the bottom of a conical iron crucible, protected throughout by a lining of loam mixed with powdered coke. The cover of the crucible is traversed by a funnel through which the metal is poured, and has a small hole for the escape of air. The metal falls on a perforated plate coated like the crucible, and placed midway between the bottom and the cover, thus presenting a body of metal to absorb the escaping phosphorus vapour.

The proportion of phosphorus required varies with the dryness of the copper after fusion. At Chatham Dockyard, where the process has for some time been used with great success, 1 cwt. of the copper phosphide is added to a charge of 5 tons, and with

this quantity the copper is scarcely ever overpoled. It represents about 0.07 per cent. of phosphorus, and about half that quantity is found to be permanently retained.

The advantages of the use of phosphorus are as follows :

1. Increased density of the metal, that of ordinary cake-copper being 8.885 to 8.839, and that of copper refined by the phosphorus process, 8.854.
2. Acceleration of the poling process and reduced consumption of poles (W. Weston, *Phil. Mag.* [4], 1. 542).

Reactions of Copper with Water and Saline Solutions.—Distilled water containing carbonic acid dissolves a notable quantity of copper, the amount increasing with the duration of the action, and the pressure under which the water has been saturated. The solvent action of water is increased by the presence of chlorides and nitrates, but diminished by that of carbonates, and to such an extent, that when carbonates are present, together with chlorides and nitrates, the solvent action of the water disappears almost entirely (Muir, *Chem. News*, xxxiv. 223, 234).

Carnelley (*Chem. Soc. J.* 1876, ii. 1) finds that the action of water on copper, very slight in itself, increases with the duration of the action, and the extent of metal-surface exposed, and is diminished by the presence of electropositive substances, and by rise of temperature. Among salts, the most active are the ammonium salts, especially the chloride; and among salts with fixed base, the action is determined mainly by the acid radicle. The least action is exerted by the nitrates, then follow sulphates, carbonates, and chlorides. In this case also the quantity of copper dissolved increases with the duration of the action, the extent of copper-surface exposed, and the concentration of the solution. With regard to the action of mixed solutions, it is found that the action of sodium chloride is somewhat increased by the presence of potassium nitrate, and in a greater degree by that of potassium sulphate. The action of ammonium sulphate is but slightly increased, and that of ammonium nitrate is neither increased nor diminished by the presence of potassium nitrate. The action of ammonium chloride is diminished, by the presence of sodium chloride, less by that of potassium nitrate, still less by that of potassium sulphate.

Sulphuration of Copper by a Mineral Water.—In the cleansing of the subterranean reservoir which receives, from a fissure in the rock, the thermal waters of Bourbonne-les-Bains, Roman coins were discovered encrusted with copper sulphide, by the slow action of the sulphates of the water and organic matters. Some of the coins had been completely sulphurised; others retained in the centre a thin remnant of the copper, which was immediately covered by a black layer of sulphide, and this was surrounded by phillipsite, while on the exterior was a stratum of copper pyrites, in which grains of sand were imbedded. The sulphide of copper first formed must have absorbed successive quantities of iron sulphide, produced under the same influences as itself, so as to change it from the intermediate condition of phillipsite to the extreme one of copper pyrites, the action being of a nature analogous to that by which iron is converted into steel by cementation. Between the layer of copper sulphide and that of phillipsite on one of these coins was found a deposit of strontium sulphate. A mass of iron pyrites was also discovered, with some vestiges of an iron bar enclosed in a cavity having the original form of the bar (De Gouvenain, *Compt. rend.* lxxx. 1297).

On the reactions of Copper salts with Phosphorous and Hypophosphorous acids, see 2nd Suppl. 966.

Action of Fatty Oils upon Copper.—This action has been studied by W. Thomson (*Chem. News*, xxxiv. 176, 200, 213). Strips of copper were immersed in various fatty oils for ten months, wholly in the first series of experiments, partially in the second. A portion of the oil was then tested for copper; another portion was warmed and shaken with water, and the water tested for copper and for acid. The general results were as follows :

1. The amount of acid in the water bore no relation to the amount of copper dissolved by the oil.
2. When the quantity of copper dissolved was large, the quantity going into solution in the water was also generally large.
3. Certain oils caused the formation of a green sediment upon the copper; little or no copper was dissolved by these oils. No fish oil, except American sperm-oil, produced a deposit on the copper.

The following oils produced sediments:—Olive; palm; palm-nut; foreign nest-foot; English ditto; tallow. Series II. Olive; palm-nut; ground nut; American tallow; common tallow; lard. Pale and brown rapeseed produced deposits only at the point where the copper came into contact with the surface of the oil. American

sperm produced a slight green deposit at the surface of the oil. North American neatsfoot covered the copper with a network of green deposit.

The following oils dissolved much copper, without causing any deposits:—Series I. Refined rape; linseed; raw cod-liver; Newfoundland cod; common seal; pale rape; American sperm; pale seal. Brown rape, castor, raw linseed, and English neatsfoot tarnished the copper, and simultaneously dissolved large quantities of the metal.

The following oils dissolved smaller quantities of copper, without producing any deposits:—Seal; pale seal; whale; cod; shark; East Indian fish.

The following produced a dark-coloured deposit on the copper:—Non-refined rape; pale cotton-seed; ordinary cotton-seed; almond. Series II. Raw linseed; English neatsfoot; cotton-seed; brown rape. Three mineral oils produced in both series a greyish deposit. English neatsfoot and tallow alluded to in Series I. dissolved no copper. In Series II. American tallow, common tallow, palm-nut oil, whale oil, and one sample of olive oil dissolved no copper.

The green deposit formed on the copper appears to contain a fatty acid.

Effect of certain Organic Bodies in Preventing the Precipitation of Copper-salts by Alkalis.—The power of preventing the precipitation of cupric hydrate by alkalis, which is exhibited by aromatic oxyacids and by phenols, appears to be limited to those which belong to the ortho-series; thus, in presence of salicylic acid, pyrocatechin, gallic acid, pyrogallie acid, quinic acid, &c., the addition of caustic soda to a cupric solution produces merely a blue-green liquid, from which not a trace of copper is thrown down, even by a large excess of the alkali. On the other hand, oxybenzoic acid, paroxybenzoic acid, resorcin, and hydroquinone, do not interfere in the slightest degree with the precipitation of the copper (Weith, *Deut. Chem. Ges. Ber.* ix. 342).

Detection of Copper. Very minute traces of copper may be detected by immersing a small couple of zinc and platinum wire in the solution to be tested, and then exposing the platinum wire to the mixed vapours of bromine and hydrobromic acid given off on treating potassium bromide with strong sulphuric acid. If the smallest trace of copper has been deposited on the platinum, a deep violet coloration will then be produced, due to the formation of a compound of hydrated copper bromide with hydrobromic acid. The tint may be conveniently observed by touching a white porcelain plate with the point of the moist platinum wire; and after the experiment, the wire may be heated in the flame of a Bunsen burner to show the green copper-flame (L. Cresti, *Gazz. chim. ital.* vii. 220).

The presence of small quantities of copper in vinegar—due, perhaps, to the action of the vinegar on the brass taps and fittings of the store-vessels—may be easily detected by electrolysis the liquid mixed with nitric or sulphuric acid in a platinum crucible serving as the positive pole of a small voltaic battery, the negative pole being formed of a bent piece of platinum-foil dipping into the liquid. The copper is then precipitated on the platinum-foil in the form of a pure red film. The deposition is accelerated by heating the crucible in water to 60°–80° (A. Roche, *J. Pharm. Chim.* [4], xxvi. 23; *Chem. Soc. J.* 1877, ii. 927).

On the Detection of Copper in the Human Body, see Raoult & Breton (*Compt. rend.* lxxxv. 40; *Chem. Soc. J.* 1877, ii. 928).

Estimation of Copper. P. Lagrange (*Ann. Chim. Phys.* [5], iii. 478) estimates copper volumetrically by decomposing it with glucose in alkaline solution. An acid copper-solution is first precipitated with excess of alkali; the well-washed precipitate is dissolved in sodium tartrate and caustic soda, and the liquid is titrated with a standard solution of glucose. To prepare this solution, a known quantity of cane-sugar, thoroughly washed with alcohol, is dissolved in a small quantity of water, and inverted by boiling with a few drops of sulphuric acid, the acid being then removed by digestion with barium carbonate. In applying this method to ores or alloys rich in iron, the iron must first be removed, which is best done by means of ammonia. The presence of silver has no influence on the determination, as this metal remains undissolved in the form of oxide, when the cupric oxide is dissolved in the alkaline solution of sodium tartrate.

Carnelley (*Chem. News*, xxxii. 308) estimates small quantities of copper colorimetrically, by comparing the brown-red colour produced in a solution of potassium ferrocyanide containing ammonium nitrate by a copper-solution of definite strength, with that which is produced under similar conditions by the copper-solution under examination.

Loss of Copper in the Cornish method of Assaying.—According to C. Mahony (*Chem. News*, xxvi. 243), the results obtained by this method are always too low, owing to loss of copper by volatilisation in the form of chloride.

This loss of copper takes place in the fusion for 'coarse-metal' and 'refining of regulus.' It is due to the circumstance that the copper oxides are reduced, and the crude button of metal subsequently refined in presence of a large proportion of sodium chloride, when, owing to the high temperature at which the reduction is effected, a small quantity of copper chloride is formed and volatilised.

The following table shows the loss actually sustained in the dry assay of three samples of copper pyrites:—

Percentage from Button	Percentage in Slag	Total percentage	Percentage by Wet Assay	Loss
10.12	0.07	10.19	11.26	1.06
8.88	0.12	9.00	10.20	1.20
13.88	0.27	14.15	15.00	0.85

According to J. Roskell, on the other hand (*ibid.* xxxiii. 77), the presence of sodium chloride is not the sole cause of loss in this method of assaying, as a volatilisation of copper takes place even when no salt of any kind is present. In the latter case, however, the loss is insignificant.

Determination of Copper and Nickel by Electrolysis.—The solution to be electrolysed is placed in a platinum crucible forming the negative electrode, and having in its axis a platinum wire twisted like a corkscrew, and forming the positive electrode; this wire passes through the perforated porcelain lid of the crucible. For the estimation of copper, the solution must be strongly acid; for nickel, ammoniacal. This method may be used for the separation of copper and nickel. The solution containing the two metals is strongly acidulated with hydrochloric or sulphuric acid, and the copper precipitated from the acid solution; the liquid is then made alkaline with ammonia, and the nickel is reduced. A battery of two or three Grove's elements is sufficient for the purpose. When a solution of German silver is analysed in this manner, the lead contained in the alloy collects in the form of peroxide at the positive pole, and the iron is precipitated by the ammonia (Merrick, *Chem. News*, xxiv. 100, 172; Herpin, *Dingl. pol. J.* cxxv. 440).

Estimation of Impurities in Commercial Copper.—The following electrolytic method is described by W. Hampe (*Zeitschr. Anal. Chem.* 1874, 176). About 25 grams of clean copper shavings are dissolved in a mixture of about 200 c.c. water and 175–180 grams of nitric acid, sp. gr. 1.2, till no trace of metallic residue is visible; filings are not so well adapted for the assay, as they are apt to be contaminated with iron and grease. The solution, whether clear or—as frequently happens—containing a suspended precipitate, is mixed with 25 c.c. of chemically pure sulphuric acid, evaporated to dryness over the water-bath, and the residue is heated in an air-bath till the small excess of sulphuric acid is completely driven off. The residue, when quite cold, is treated with 20 c.c. nitric acid, sp. gr. 1.2; 350 grams of water are gradually added till the whole of the cupric sulphate is dissolved; and hydrochloric acid is added in quantity just sufficient to precipitate the silver contained in the solution. The precipitate, consisting of silver chloride, together with lead sulphate and antimonious acid or antimonates which have remained undissolved, is collected on a very small filter, and the solution, together with the wash-water, is electrolysed till all the copper is precipitated, the precipitation being complete when a fresh platinum electrode introduced into the liquid becomes covered with a mere shade of metallic copper. The liquid is then drawn off with a syphon, without interrupting the current, and replaced as it flows off by water directed from wash-bottles on the electrodes, till the evolution of gas at the positive pole ceases, a sign that the liquid no longer has any acid reaction. The current is now interrupted; the platinum cone which serves for the negative electrode with its adhering film of copper, is again washed with water, then over another vessel with alcohol; and the copper is dried by holding it in the hot air over a heated platinum of silver dish, and lastly weighed. The platinum spiral forming the positive electrode, on which a coating of lead dioxide is always deposited, is rinsed in like manner; and the liquid, amounting to about 4 liters, is strongly concentrated in a flask, and finally evaporated nearly to dryness in an air-bath. The residue is warmed with strong hydrochloric acid; the resulting solution diluted with water, and filtered from a small quantity of silica derived from the glass vessels; and the filtrate is several times treated with hydrogen sulphide, to ensure the complete precipitation of arsenic. Before filtering off this precipitate the lead dioxide deposited on the platinum spiral is dissolved in hydrochloric acid; the lead precipitated as sulphate by addition of sulphuric acid; and the precipitate, together with the sulphide of arsenic, is collected on the same filter with the silver chloride, antimonates, &c., previously separated. The filtrate serves for the determination of iron, nickel, &c.

The mixture of silver chloride, lead sulphates, antimonates, &c., is fused, after

destruction of the filter, with sodium carbonate and sulphur, whereby the antimonates are completely decomposed; the melt is digested with water till it is completely disintegrated; the hot solution is passed through the filter which contains the precipitates separated by hydrogen sulphide from the other filtrates; and this filter is washed, first with dilute solution of potassium sulphide, then with sulphuretted hydrogen water, whereby the whole of the arsenic, antimony, and tin are obtained, in the filtrate as sulphur-salts, while the lead, silver, bismuth, and copper remain in the residue, and may be separated by known methods.

To determine the iron, cobalt, nickel, &c., the filtrate from the sulphuretted hydrogen precipitate is oxidised with nitric acid, the iron is precipitated by ammonia, and the cobalt and nickel from the ammoniacal filtrate by electrolysis.

Lastly it must be remembered that bismuth, if present, is completely dissolved in the treatment of the copper with nitric acid, and precipitated, together with the copper, by the electric current: hence it is necessary to submit the electrically deposited copper to a special examination. For this purpose, the bismuthiferous copper is dissolved in a sufficient quantity of nitric acid; the solution mixed with a large excess of hydrochloric acid, and boiled till all the nitric acid is expelled, and the contents of the flask consist wholly of metallic chlorides; and the liquid, after concentration on the water-bath, is mixed with a large quantity of boiling water, whereby the whole of the bismuth is thrown down mixed with a small quantity of basic copper salt, and the two metals are separated by means of ammonium carbonate.

To determine whether the foregoing metals are present wholly or partly in the reguline state, or in the form of oxides or salts, two series of experiments are required, namely, the quantitative analysis of the residues obtained: (1) by treating the copper with nitric acid; (2) by treating it with neutral silver nitrate. The first of these residues contains the metals which are present in the copper as antimonates, especially bismuth, lead, nickel, copper (as cuprous salt), &c. The residue left on treating the copper with silver nitrate, contains arsenic, lead, and iron, together with cobalt and nickel, if these metals were present in the copper as oxides or as sal.

The total quantity of oxygen is best estimated by reduction with hydrogen and determination of the loss of weight, or of the quantity of water formed. To determine the quantity of oxygen present as cuprous oxide, the copper is treated with neutral silver nitrate, whereby a mixture of silver and basic cupric salt is precipitated, and the quantity of copper in this precipitate gives by calculation the amount of cuprous oxide originally present.

COMPOUNDS OF COPPER.

Alloys. 1. With silver. The melting points of a series of copper-silver alloys have been determined by W. C. Roberts (*Proc. Roy. Soc.* xxiii. 349, 481) by the method of Pouillet (*Éléments de Physique*, 6me. Ed. ii. 564), which consists in plunging into the just melted alloy a wrought-iron cylinder of known weight and specific heat. The crucible containing the melted alloy is then removed from the fire, and when the alloy shows signs of solidifying, the iron is immediately transferred to a water-calorimeter, and the rise of temperature of the water observed. From this, together with the weight and specific heat of the iron, the melting point of the alloy may be calculated by means of a formula to be presently given.

First, however, it is necessary to determine the mean specific heat of the iron cylinder between 0° C. and a known point near the maximum temperature likely to be attained in the course of the experiments. A convenient temperature for the purpose is the melting point of silver, which Becquerel determined by placing a wire of pure silver in a crucible enclosed in a porcelain tube surrounded by the vapour of boiling zinc, and therefore at a temperature of 1040°. This heat is sufficient to effect the partial fusion of the silver, the melting point of which is therefore also 1040°.

This temperature being known, the specific heat x of the iron is given by the equation:

$$x = \frac{(P + p'c' + p''c'')(t - t_0)}{p(T - t_0)}$$

Where p is the corrected weight of the iron cylinder; *
 P that of the water;

* In transferring the iron cylinder from the crucible to the calorimeter it is impossible to avoid carrying over a small quantity of the melted metal which adheres to the iron: this has to be allowed for. With pure silver, 0.06701 may be taken as the specific heat, and in the case of alloys, the necessary correction may be made by deducting the specific heat of each alloy from the specific heats of its constituents; and the weight of iron equivalent to that of the metal or alloy carried over is calculated by multiplying the weight of transferred metal by its specific heat, and dividing the product by the specific heat of iron, as ascertained by preliminary experiments. This weight is then added to that of the iron employed.

COPPER-SILVER ALLOYS.

$p'c'$ and $p''c''$ the water-equivalents of the calorimeter and thermometer respectively;

t , the initial temperature of the water;

Θ , the final temperature of the water;

T , the initial temperature of the iron, and therefore the melting point of the metal [in this case = 1040°];

x , the specific heat of the iron.

In one experiment these quantities had the following values:

$$\begin{array}{lll} p & = & 84.446 \text{ grams} & T & = & 1040^\circ \\ P & = & 260.520 & t & = & 16^\circ \\ p'c' + p''c'' & = & 15.687 & \Theta & = & 63^\circ \end{array}$$

These values substituted in the preceding equation give:

$$x = \frac{(260.52 + 15.687)(63 + 16)}{84.446(1040 + 63)} = 0.15734.$$

The mean of three successive experiments gave 0.15693.

The several alloys were prepared by melting together pure silver and pure copper, and, as soon as the crucible containing the fused metal was withdrawn from the furnace, a small portion of the thoroughly fused alloy was granulated and set aside for analysis.

The data for ascertaining the melting point of each alloy were furnished by an experiment similar to that which was made for determining the specific heat of the iron, and the result was calculated by transposing the equation above given, making T the unknown quantity instead of x . The equation then becomes:

$$T = \frac{(P + p'c' + p''c'')(\Theta - t) + \Theta}{px}$$

the value assigned to x being in all cases 0.15693, as above determined.

The results are given in the following table.

Melting points of Silver-Copper Alloys.

No.	Parts of pure silver in 1000 parts of the alloy	Approximate formula	Melting points (mean) in degrees Centigrade
1	1000 (pure silver)		1010
2	925	Ag^7Cu	981.1
3	820.7	Ag^6Cu	886.2
4	798	$\text{Ag}^{5.5}\text{Cu}^{0.5}$	887.0
5	773.6	Ag^5Cu	858.3
6	750.3	Ag^4Cu^2	850.4
7	718.93	Ag^3Cu^2	870.5
8	630.20	AgCu	846.8
9	600	Ag^2Cu^3	857.0
10	569.6	Ag^2Cu^3	899.9
11	561.1	Ag^2Cu^3	917.6
12	540.8	$\text{Ag}^{2.5}\text{Cu}^{2.5}$	919.8
13	500	Ag^2Cu^3	940.8
14	497	$\text{Ag}^{2.5}\text{Cu}^{2.5}$	962.6
15	459.4	AgCu^2	960.8
16	250.5	AgCu^4	1114.1
17	0 (pure copper)		1330

The alloys numbered 7 and 8 are of especial interest. The first, Ag^3Cu^2 , is Levol's homogeneous alloy (v. 287), which does not exhibit the phenomenon of liquation, but retains its constitution when slowly cooled. The alloy AgCu , in which the atomic relation between the two metals is the simplest of all, exhibits the lowest melting point.

In studying the phenomena of liquation, the alloys were cast in red-hot moulds of fire-brick, in which the metal (about 50 oz.) could be slowly and uniformly cooled. The results showed that the homogeneity of Levol's alloy is slightly disturbed by this method of casting; and, on the other hand, that alloys which contain more than 71.89 per cent. of silver hardly show signs of rearrangement when the solidification takes place gradually. Two alloys containing respectively 63 and 33.3 per cent. of silver

were found to be far from homogeneous, and in the former the arrangement was influenced by gravity, the base of the casting being rich in silver.

The specific gravity of Leval's alloy was found to be 9.9045 in the solid and 9.0054 in the fluid state.

2. With Tin. A Riche (*Ann. Chim. Phys.* [4], xxx. 351) has examined a series of these alloys with regard to fusibility, liquation, and changes of density resulting from certain operations. The alloys SnCu^1 and SnCu^4 are the only ones which melt and solidify without decomposition, and their melting points lie between those of antimony and of silver (of 899 degrees of fineness), or about $600^\circ\text{--}700^\circ$; all other alloys of tin and copper undergo liquation at the moment of solidification.

To examine these phenomena more closely, the several alloys, in quantities of 500 to 700 grams, were fused for ten hours in tubular moulds, and the top and bottom portions of the castings were analysed. Another portion of each of the melted alloys was stirred during solidification, and the portion which last remained fluid was poured off and likewise analysed. The results are given in the following table:

Composition of the alloy	Percentage of tin		Percentage of tin of the portion last solidified	Physical properties
	top	bottom		
1. { Cu 9.73 Sn 90.27 }	87.87	92.90	98.50	{ tin-grey, soft as tin; non-crystalline
2. { Cu 15.21 Sn 84.79 }	83.15	78.90	96.99	{ tin-grey, crystallising by slow cooling
3. { Cu 21.21 Sn 78.79 }	81.81 74.97	84.56 77.40	94.40	{ tin-grey, crystallised, moderately hard
4. { Cu 34.99 Sn 65.01 }	58.11 55	75.83 80	82.83	{ whitish-grey, crystalline, brittle
5. { Cu ² 51.84 Sn 48.16 }	—	—	50.42	{ bluish-grey, like zinc; crystalline, very brittle
6. { Cu ³ 61.79 Sn 38.21 }	37.29	37.66	37.37 to 37.33	{ bluish, fine-grained, pulverisable in the mortar
7. { Cu ⁴ 68.28 Sn 31.72 }	30.44	30.83	30.91	{ white, laminar, brittle as glass
8. { Cu ⁵ 72.91 Sn 27.09 }	27.15	26.78	27.76	{ white, with yellowish reflex; crystalline, very hard
9. { Cu ⁶ 76.31 Sn 23.69 }	23.37	23.69	25.17	{ yellowish, very hard, fine-grained; malleable at dull red heat
10. { Cu ⁷ 79.02 Sn 20.98 }	21.00	21.32	24.85	like No. 9
11. { Cu ⁸ 81.85 Sn 18.15 }	18.88	13.56	24.60	like No. 9
12. { Cu ¹⁰ 85.67 Sn 14.33 }			20.06 24.50	distinctly yellow
13. { Cu ¹⁵ 89.00 Sn 11.00 }			13.10	gun-metal

The specific gravity of these alloys is best determined by filing off portions from the upper and lower ends of the casting, and taking the mean of the two specific gravities. In alloys rich in tin expansion takes place (that is to say, the specific gravity of the alloy is less than the mean specific gravities of the two metals), up to the proportion CuSn^2 ; alloys richer in copper exhibit contraction, which is small in the alloy SnCu^2 , then suddenly becomes very great, attains its maximum in SnCu^4 , and then gradually diminishes. The greatest density, 8.91, is found in the alloy SnCu^4 , even the more cupriforous alloys exhibiting lower densities, e.g. gun-metal, 8.84.

The hardness of the alloys, reckoning from pure tin, increases with the proportion of copper up to CuSn . This, and all the more cupriforous alloys up to Cu^4Sn , are extremely brittle, and from this alloy the hardness diminishes as the proportion of copper increases.

The alloy SnCu^a is distinguished from all the rest by several characters: it presents the same homogeneous composition after repeated fusion, is peculiar in colour, has the highest density, exhibits the greatest degree of contraction, and is so brittle that it may be pounded in a mortar.

Bronzes rich in tin (18 to 22 per cent.), such as are used for making wind-instruments, have their density increased by ignition and sudden plunging into cold water; but on again raising them to a red heat, and then leaving them to cool slowly, the density is lowered, but not to the value which it had before the sudden cooling. By mechanical treatment, such as simple compression or the blow of a coining press, followed either by sudden or by slow cooling, the density of these alloys is increased, more also (from 8.775 to 8.952) by pressure and sudden cooling, than by pressure and slow cooling (from 8.782 to 8.854). These bronzes, therefore, are affected by sudden cooling, and by annealing, in the opposite manner to steel. They cannot be worked at ordinary temperatures, because they break too easily; they are likewise brittle at a red heat, and between 100° and 200° . But at temperatures a little below dull redness they may be forged like bar-iron, easily hammered out into thin plates, and reduced from 14 mm. to 1 or 2 mm. thickness by passing between rollers. This property renders them available for the fabrication of gongs, which in external appearance and sonorous quality, as well as in chemical composition, are identical with the famous Chinese instruments. By the same treatment in the warm state these bronzes are moreover rendered denser, and more easily brought up to any given density, than by similar treatment when cold.

Alloys containing a smaller proportion of tin (94 to 88 per cent. copper and 6 to 12 per cent. tin) which can be rolled and hammered at ordinary temperatures (gun-metal, &c.), are not increased in density by cooling either slow or sudden. If they are at the same time subjected to mechanical treatment their specific gravity is slightly increased. A bronze containing 6 per cent. tin had its density increased from 8.924 to 8.932 by 72 blows, alternating with 24 annealings, and by similar treatment, substituting quick for slow cooling, the density was increased from 8.928 to 8.935.

Riche has also studied the liquation of gun-metal. Analyses of samples taken from the outer and inner layers of a gun at different distances from the breech showed that the portion of the alloy near the axis of the bore is not homogeneous, but contains white crystalline grains very rich in tin (11.21 to 14.49 per cent.).

On the whole, however, the outer layers are richer in tin (containing 9.282-9.676 per cent.) than the inner, which contain from 8.726 to 9.046 per cent. tin. For the striking of bronze medals an alloy containing 96.97 per cent. copper and 4 per cent. tin is well adapted by its colour, ring, and facility of working (Riche).

Specimens of Chinese and Japanese bronze, distinguished by a very beautiful dull black colour (*patina*), have been analysed by H. Morin (*Compt. rend.* lxxviii. 811) with the following results:

	1	2	3	4	5	6	7
Tin	4.36	2.64	3.27	3.23	5.52	7.27	6.02
Copper	82.72	82.90	81.30	83.09	72.09	73.32	71.46
Lead	9.90	10.46	11.05	11.50	20.31	14.59	16.34
Gold	—	trace	—	—	—	—	—
Iron	0.55	0.64	0.67	0.22	1.73	0.28	0.25
Nickel	—	trace	—	—	—	—	—
Zinc	1.86	2.74	3.27	0.50	0.67	6.00	5.94
Arsenic	trace	0.25	trace	0.25	trace	trace	trace
Sulphur	trace	—	—	trace	trace	—	—
	99.39	99.63	99.56	98.79	100.32	100.46	100.01

No. 1 has a specific gravity of 8.8455.

The peculiar black colour of these bronzes is not due to superficial sulphuration, but belongs to the substance of the bronze. It increases indeed in intensity with the proportion of lead present, which in all these specimens is larger than in ordinary bronze. The presence of zinc rather impairs the colour.

In imitation of these bronzes, alloys were made of the following composition:—

	Sn	Cu	Pb	Fe	Zn
I.	6.5	72.5	20.0	1.5	0.5
II.	5.0	83.0	10.0	—	2.0

No. I. produced an alloy exceedingly difficult to work, and, without giving any superior results as regards colour, furnished castings which were extremely brittle.

No. II., on the contrary, gave an alloy exactly resembling the Chinese bronze. Its fracture and polish were identical, and, when heated in a muffle, it quickly assumed the peculiar dead-black appearance, so greatly admired in the Chinese specimens. Hitherto it has been found difficult, if not impossible, to obtain this depth of colour with bronzes of modern art, since the surface scales off when heated under similar conditions.

Christophle and Bouillet (*Compt. rend.* lxxviii. 1019) confirm the results of Morin's analyses, but point out that the presence of lead in bronze is by no means essential to the production of a fine black patina. By peculiar oxidation-processes they profess to have succeeded in producing brown, orange-yellow, red and black patina on pure copper. These processes are not fully described, but are said to consist in the production of cuprous oxide in two molecular states, and of copper sulphide.

Two Japanese bronzes, having the colour of brass, were found by S. Kalischer (*Dingl. pol. J.* cxxv. 93) to contain :

		Cu	Pb	Zn	Fe	
I.	4.38	76.60	11.88	6.53	0.47	99.86
II.	4.36	76.53	12.29	6.58	0.33	100.09

Specimens of Japanese bronze have also been analysed by Maumené (*Compt. rend.* lxxx. 1009) with the following results :

	1	2	3	4
	86.38	80.91	88.70	92.07
	1.94	7.55	2.58	1.04
Antimony	1.61	0.44	0.10	—
Lead	5.68	5.33	3.54	—
Zinc	3.36	3.08	3.71	2.65
Iron	0.69	1.43	1.07	3.64
Manganese	—	trace	—	—
Silica	0.10	0.16	0.09	0.04
Sulphur	—	0.31	—	—
Loss	0.26	0.79	0.21	0.56

The specimens were from 5-12 mm. thick, hard or granular texture, with small cavities in the interior, smooth on the outside. The alloys were probably not made by melting the metals together, but prepared directly from ores.

The following analyses of antique bronzes have been made by Flight (*Dout. Chem. Ges. Ber.* vii. 1461):

	1	2	3	4
Copper	97.226	93.398	99.470	88.771
Iron	0.322	0.729	0.384	0.476
Cobalt	—	—	—	0.304
Nickel	—	0.153	0.084	trace
Gold	0.279	0.305	—	—
Lead	0.076	—	—	1.504
Tin	trace	—	—	8.508
Arsenic	1.348	trace	trace	—
Sulphur	—	0.305	—	—
Phosphorus	trace	trace	trace	trace

1 to 3 are spears from Cyprus.

4 is a fragment of a dagger.

Phosphorus-bronze.—The addition of phosphorus during the melting together of copper and tin improves the physical qualities of the bronze in several respects. This was noticed by Parker in 1858, and subsequently by Percy, Will, Abel and others (*Dingl. pol. J.* ccli. 381). According to Montefiori-Levy, and Künzel (*ibid.* cc. 379) the phosphorus acts either by preventing the oxidation of the metals, or by converting the oxides into a phosphoretted slag, so that the tenacity of the alloy is no

longer impaired by the interposition of oxides between its molecules. In the ing of phosphorus-bronze, the copper is more oxidised than the tin, and the partly united with phosphorus, forming a compound containing 2 at. phosphorus and 9 at. tin. The colour of the bronze, thus produced, is warmer than that of ordinary bronze, more like that of gold containing copper; its grain resembles that of steel; its elasticity is greater by 80 per cent., and its absolute tenacity by 170 per cent. than that of ordinary bronze. Phosphorus bronze is very hard, very fluid when melted, fills up the moulds well, and yields very homogeneous castings, so that it is well adapted for the manufacture of gun-barrels, and of axle-beds for machinery.

Experiments made in the Polytechnic School (*Gewerbakademie*) at Berlin, on the tenacity of phosphorus-bronze, showed that a rod of this bronze loaded with 200 centners per cubic inch broke only after 408,230 extensions, whereas good ordinary bronze, equally loaded, bore only 420 extensions. Under the same tension, phosphorus-bronze broke after 862,980 flexures, ordinary bronze after 102,650. The following results were obtained by R. Jenny, in Vienna:

Modulus of elasticity for longitudinal tension	Tenacity of extension at the limit of elasticity	Tenacity of extension at the limit of fracture
5587 kg. per sq. mm.	13.74 kg. per sq. mm.	40.40 kg. per sq. mm.

With phosphorus-bronze for guns, Uchatius obtained the following results:

	Absolute tenacity kg. per sq. cm.	Limit of elasticity kg. per sq. cm.	Extension per cent.
Phosphorus-bronze No. 4	3600 to 3340	600 to 400	20.66 to 14.66
" " No. 5	5660 to 5540	3800 to 2800	1.6 to 2.28
Krupp's steel for guns	5000	1000	11
Normal gun-metal	2200	385	15

According to D. Kirkaldy (*ibid.*) sheathing plates for ships, made of pl. bronze, lost, by six months' immersion in sea-water, 1.158 per cent. of their weight, whereas copper-sheathing under similar circumstances lost 3.058 per cent.

On the properties and uses of Phosphorus-bronze, see also Montefiori-Levy, and Künzel (*Dingl. pol. J.* cxxi. 372); G. Montefiori-Levy (*American Chemist*, v. 178).

3. **Copper and Zinc.** The formation of these alloys is attended with contraction, which attains its maximum in the compounds Zn^3Cu^2 and Zn^2Cu . These alloys are brittle, like SnCu^3 and SnCu^4 , and exhibit none of the physical properties of the unalloyed metals. Zn^2Cu has a sp. gr. of 8.048 (calc. 7.679); Zn^3Cu^2 has a sp. gr. of 8.171 (calc. 7.783). The density of brass is increased by mechanical treatment, but this effect is partly annulled by sudden, and still more by slow cooling. Pinchbeck is not altered in density, either by working or by cooling either slow or sudden. The same is the case with aluminium bronze containing 10 to 5 per cent. aluminium (Riche, *Ann. Chim. Phys.* [4], xxx.)

4. **Copper and Iron.** The addition of iron to copper diminishes its porosity and increases its toughness and elasticity. Copper and iron do not easily alloy together, the cast bars being richer in iron at the top than at the bottom. An alloy containing 4.5 per cent. iron has a sp. gr. of 8.885, and yields a homogeneous casting; but on leaving it at rest for some time in the fused state, an alloy containing 6 per cent. iron collects at the top of the casting, while the lower part contains only 4 per cent. The hardness and tenacity of copper are increased by addition of iron.

Chlorides. *Sensitivity to Light.*—Carlemann (*J. pr. Chem.* lxxxv. 478) observed that a plate of copper exposed to the action of chlorine gas till it becomes yellow, blue, red, yellow, and finally again blue, or treated with a solution of cuprous chloride in hydrochloric acid till it assumes a light brown-red tint, becomes so sensitive to light that photographs may be taken upon it, the parts on which the light falls turning black. The photographs, if kept in the dark, remain distinct for months, but ultimately fade. According to Priwoznik (*Dingl. pol. J.* cxxi. 38) a solution of cuprous chloride does not produce this effect unless it has been partly converted into cupric chloride by the action of the air. He finds, also, that the best way of rendering a copper-plate sensitive to light, is to dip it into a neutral and only slightly diluted solution of cupric chloride, and thinks it very likely that the sensitiveness is due to a thin film of cuprous chloride, this compound in the moist state being known to become coloured by the action of light. Alloys of copper with silver, manganese, and zinc may also be rendered sensitive to light by similar treatment, but in a much lower degree than pure copper; in fact this difference of behaviour may be used as a ready means of testing the purity of copper.

Oxides. *Action of Ether on Cupric Oxide.*—When dry cupric oxide obtained by precipitation is heated in anhydrous ethyl oxide to 280° in a sealed tube, it is con-

verted into a yellow mass, from which hydrochloric acid dissolves out a small quantity of cuprous hydrate, leaving metallic copper as principal constituent. The ether is at the same time oxidised to aldehyde and acetic acid. On the other hand, when black cupric oxide obtained by precipitation is heated with ether and a little water, it is reduced to red cupric oxide, likewise with formation of aldehyde and acetic acid, the latter, however, in smaller proportion than before. Black cupric oxide prepared in the dry way is not reduced by ether at the temperature above mentioned (Guérout, *Compt. rend.* lxxix. 221). Guérout had formerly observed, in conjunction with Becquerel, that artificial *malachite* is reduced to cuprous oxide by ether at 280°.

Phosphides. Copper phosphide is easily prepared by lining a crucible with a mixture of 14 pts. silica, 18 pts. bone-ash, 4 pts. powdered coal, 4 pts. sodium carbonate, and 4 pts. glass powder, made up into a paste with gum-water; then adding granulated copper; covering this with a layer of the mixture; and closing the crucible with a well-fitting lid. Soda-glass or milk-glass may also be added, the former to facilitate the fusion, the latter to line and cover the crucible. On fusing the mixture at a strong heat, the silica acts on the phosphate, taking away the base, and the phosphoric acid, as fast as it is liberated, is reduced by the coal, the phosphorus set free then uniting with the copper (H. Schwarz, *Dingl. pol. J.* ccxviii. 58).

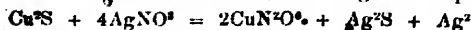
Montefiori-Levy and Künzel prepare copper phosphide for the manufacture of phosphorus-bronze, by putting sticks of phosphorus into crucibles containing the melted copper. To avoid a too-ready combustion, the sticks of phosphorus are coated with a firm layer of copper by placing them in a solution of cupric sulphate. The quantity of phosphorus penetrating the bronze is but very small; 0.5 per cent. is said to be sufficient; still a considerable quantity of phosphorus is always wasted. This might be prevented by filling a clay tube, closed at one end, with sticks of phosphorus coated with copper or with powdered red phosphorus, and dropping the tube its open end into the melted copper. If the tube is pressed to the bottom of the tube, the vapours of phosphorus can escape only after having passed through a layer of the melted copper.

Sidot (*Compt. rend.* lxxiv. 1454) describes the preparation of a phosphide of copper by the action of phosphorus on a solution of copper sulphate. It is a black substance, of sp. gr. 6.35, not changed by air or water. At a red heat it melts, losing about 10 per cent. of its weight, and forming when cold a greyish-white, brittle, metallic-looking substance. If, however, the heat be greatly raised, phosphorus is expelled, and the mass on cooling is white, and as hard as steel. When it has been several times fused and cast in ingots at different temperatures, it acquires very marked sonorous properties, especially if a little tin be added. The phosphides of copper present a ready means of incorporating known quantities of phosphorus with other metals. By heating the black phosphide in presence of phosphorus vapour, a compound is obtained in fine hexagonal crystals having a metallic lustre. Another crystallised phosphide of copper is formed, by heating in a crucible an intimate mixture of acid calcium phosphate, copper oxide, and charcoal.

Sulphides. *Cupric sulphide*, CuS , may be prepared by the action of a solution of sulphur in carbon sulphide on copper turnings, the excess of sulphur being removed by washing with carbon sulphide; also by precipitating a copper salt with potassium pentasulphide, and washing out the excess of sulphur (Champion and Pellé, *Bull. Soc. Chim.* [2], xxiv. 436).

Cuprous Sulphide, Cu_2S .—This compound is easily obtained in small crystals, resembling native copper-glance, by igniting cupric sulphide (precipitated from an acid solution by sulphuretted hydrogen) in coal-gas. If the copper sulphide contains sulphur, or arsenic sulphide intermixed with it, the crystals form with greater facility. The reason is probably this: an arsenic-copper sulphide forms in the first stage, but when the temperature increases, arsenic sulphide volatilises, and copper-glance crystals separate out. These crystals are very small, but have a strong metallic lustre, and exhibit under the microscope the combination, $\text{OP} \cdot \infty \text{P} \cdot \infty \text{P} \cdot \infty \text{P}$, with great distinctness. The crystal type is 'short prismatic' (Frenzel, *Jahrb. f. Min.* 1875, 473).

Cuprous sulphide reacts with silver nitrate, according to the equation:



(E. Schneider, *Pogg. Ann.* clii. 471).

A specimen of copper-glance from the province of Catamarca in the Argentine Republic, having a sp. gr. of 4.7, and containing imbedded crystals of quartz and iron pyrites, was found by Schinnerer (*Jahrb. f. Min.* 1872, 977) to contain:

Cu	S	Fe	As	Zn	SiO_2 (Matrix)	Bisph.
48.82	26.71	6.64	9.16	0.74	7.52	traces = 99.59

Silver copper-glance (*Strohmeyerite*), forming the principal ore of a mine on the Hoyada, in the north of Catamarca, is described by A. Stelzner (*Mineralogische Mittheilungen*, 1873, 250). It occurs in tile-ore, intergrown with small quantities of copper pyrites and galena, sometimes in the interior of nodules consisting externally of silicious malgachite with a little cerussite. An analysis by Siewert gave:

Cu	Ag	S	Insol.	Sp. gr.
31.61	52.60	14.38	1.07 = 99.66	6.15-6.19

Copper pyrites.—The ratio of the principal axis to the secondary axes of this mineral, viz. 0.98522 : 1, given by Haidinger, is confirmed by v. Kokscharow's measurements of crystals from the Victoria mine, near Müsen (*Jahresb. f. Chem.* 1874, 1257).

G. vom Rath (*Pogg. Ann. Jubelband*, 1874, 544) describes a twin-crystal of copper pyrites from Grünau on the Sieg, in which the two individuals of the combination $\frac{P}{2} \cdot - \frac{P}{2} \cdot P\infty \cdot \frac{2}{3} P\infty \cdot 0P$, are grown together by the two tetrahedral faces, but in such a manner (as shown by the different positions of 0P in the two) that the tetrahedral face of the one individual belongs to the positive, and that of the other to the negative tetrahedron.

Extraction of the Precious Metals from Copper Pyrites.—The pulverised residues are mixed with sodium chloride, and roasted in a reverberatory furnace. The roasted mass, consisting principally of ferric oxide, sodium sulphate, sodium chloride, and copper chloride, is next lixiviated with water rendered acid by hydrochloric acid. The insoluble ferric oxide is used for the fettling of puddling furnaces, while the lixivium which contains the copper, silver, and gold, as chlorides, is precipitated by addition of a soluble iodide (or a solution of kelp), as it has been found that silver iodide is much less soluble than silver chloride in a solution of sodium chloride, and that the precipitate obtained by the addition of an iodide to the lixivium contains nearly the whole of the silver, together with the gold. This precipitate is freed from copper by hydrochloric acid, and reduced by zinc, the iodide of zinc obtained being used for the precipitation of a new quantity of silver. The copper contained in the liquor from which the gold and silver have been thus separated, is precipitated by means of metallic iron.

During 1871, 16,300 tons of residue have been thus treated in the works established at Widnes by Claudet and Phillips, the yield of silver being 333,242 grams (10,715 troy ounces), and that of gold being 3,172 grams (102 troy ounces) (*P. Claudet, Ann. Chim. Phys.* [4], xxvii. 407).

COPPER-ZINC COUPLE. The activity of these couples depends partly on the proportion of copper deposited on the zinc foil, partly on its state of aggregation, which varies with the strength of the solution of copper sulphate employed to attack the zinc. If the couple is to be employed for the decomposition of water, or for preparing ethane from a mixture of alcohol and ethyl iodide, the maximum activity is obtained by depositing the copper from a 2 per cent. solution of the sulphate in six successive depositions; but, for dry couples, such as those used in the preparation of the organo-zinc compounds, and in similar reactions, one deposition from a 2 per cent. solution is found to be most effective. The chemical activity of these couples has been experimentally ascertained to be more than 2000 times as great as that of pure zinc (Gladstone & Tribe, *Chem. Soc. J.* 1877, i. 561).

COPTINE. An alkaloid, contained, together with berberine, in *Coptis trifoliata* Salisburi (the *Helleborus trifolius* of Linnaeus), a ranunculaceous plant growing in North America. Coptine is colourless, and forms with potassio-mercuric iodide a crystalline precipitate which dissolves in sulphuric acid to a colourless liquid becoming purple-red when heated. The plant also contains albumin, resin, a fatty oil, colouring matter, extractive matter, sugar, vegetable fibre, and 4 to 5 per cent. ash, one-tenth of which consists of silica (*E. Z. Gross, N. Rep. Pharm.* xxxiii. 53).

CORALLIN. See ROSOLIC ACID.

CORCHORUS. See JUTA.

CORDIERITE. The crystalline form of cordierite, occurring near Lake Leach in shaly eruptive masses, together with sanidin, biotite, sapphire, garnet, diopside, spinel, and magnetite iron ore, is described by G. vom Rath (*Pogg. Ann.* clii. 40; *Jahrb. f. Min.* 1874, 865).

On Pseudomorphs of Cordierite, see A. Wichmann (*Jahrb. f. Min.* 1875, 194).

CORUNDUM. A description of the corundum region of North Carolina, Georgia, and Montana, and of the minerals accompanying it, is given by J. L. Smith (*Sill. Am. J.* [3], vi. 180; *Compt. rend.* lxxvii. 356, 439).

The corundum of North Carolina appears in the form of blue, green, grey, pink, ruby-coloured, or white masses, sometimes weighing 300-400 kilograms. Some specimens show a cleavage-plane, and some have a hexagonal prismatic form. The gangue is either chrysolite or serpentine. The former occurs in a system of veins extending for 190 miles. Their course for 130 miles lies along the north-west side of the Blue Mountains, at a mean distance of 10 miles from the summit, from Mitchell County to Macon County. They then make a curve round the source of the Little Tennessee, and run towards the north-west for 10 miles, after which they follow the line of the Blue Mountains. The serpentine appears at intervals along the whole of this line. From Mitchell to Macon it is always found inclosed in gneiss containing rose garnet, kyanite, and pyrites. After the above-named curve it is found in both gneiss and hornblende. From Buck's Creek to the south-west the latter occurs in very large masses, in which albite replaces the ordinary felspar. Associated with the serpentine are chalcodony, magnetic oxide, chrome-iron, spinel, rutile, chromite, chlorite, talc, steatite, anthophyllite, tourmaline, emeryllite, epidote, zoisite, albite, asbestos, picrolite, actinolite, and tremolite. The corundum occurs, sometimes in ripidolite in the fissures of the serpentine, sometimes, as at Buck's Creek, in chlorite, except the red variety, which is found in zoisite. The chrysolite of North Carolina holds a position analogous to that of the calcareous rock of Asia Minor, which forms the gangue of emery in that region. The adjacent rocks in each of the localities show the formations to be of the same geological age, and contemporaneous with the formation in Chester (Mass.) Each locality has, however, its special characteristic. In Asia Minor the emery is associated with but a small quantity of black tourmaline. Diaspore is also rare, but when it does occur, it is found in most perfect crystals. The emery of Naxos and Nicaria is accompanied by black tourmaline in abundance. The rock containing the corundum of Chester is composed of talc and saponite with hornblende-gneiss. It is accompanied by magnetic iron oxide and tourmaline in abundance.

Prof. Shepard is in possession of two crystals of corundum, each weighing 150 kilograms. One of these is red on the surface and bluish-grey in the interior. Its form is that of a hexagonal prism whose summit is terminated by a rather uneven hexagonal plane. The second crystal is greyish-blue, with a pale sapphire colour near the angles. Its form is that of a regular hexagonal prism, well defined at one end only. Some of the lateral faces are coated with pearly margarite.

A very elaborate memoir on corundum, its products of decomposition, and the minerals which accompany it, has been published by F. A. Genth (*J. pr. Chem.* [2], ix. 49-113; abstr. *Jahrb. f. Chem.* 1873, 1151).

The accompanying rocks are olivine-rock and chlorite slate, which form the gangue of the corundum.

The accompanying minerals are the following:

Spinel, in pseudomorphs after corundum.	Willeoxite.
Smaragdite (?).	Pattersonite.
Zoisite.	Chloritoid.
Felspars, including andesite and oligoclase.	Margarite, and an earthy mineral produced by its transformation.
Fibrolite, pseudomorphous after corundum.	Dudleyite.
Staurolite.	Diaspore.
Damourite, frequently in pseudomorphs after corundum.	Bauxite.
Ephesite.	Gibbsite.
Paragonite.	Quartz.
Jefferisite.	Opal.
Chlorite.	Tourmalin.
Kerite.	Cyanite.
Maconite.	Pyrophyllite.
	Euphyllite.
	Lazulite.

Respecting the formation of these minerals, Genth suggests the following views: Simultaneously with the formation of the olivine-rock containing chrome-iron ore (afterwards partially converted into serpentine, &c.) alumina separated in the form of corundum. This was subsequently transformed into a large number of minerals, viz. spinel, fibrolite, cyanite, perhaps felspar, tourmalin, damourite, chlorite, and margarite. Some of these transformation-products still exist in the form of thick beds of mica-(damourite-) and chlorite-slate, whilst another portion is further transformed into pyrophyllite, bauxite, lazulite, &c.

Amongst these minerals the following are new species.

1. *Kerite* found in the Calsagee mine, Macon Co., North Carolina, consists of numerous fine scales, very mild, of sp. gr. 3.303, light greenish yellow to brownish colour, and nacreous lustre. It melts to a white enamel, and dissolves in hydrochloric acid.

The mean of two closely agreeing analyses by Chatard gave—

SiO ²	Al ² O ³	Fe ² O ³	FeO	NiO a. CoO	MgO	H ² O
38.29	11.41	1.95	0.32	0.25	26.40	21.25 = 99.87

whence may be deduced the formula $2(3\text{RO} \cdot 2\text{SiO}^2) + (\text{R}^2\text{O}^3 \cdot \text{SiO}^2) + 10\text{H}^2\text{O}$.

2. *Maconite*, from Macon Co., North Carolina, likewise forms scaly aggregates. Sp. gr. = 2.827. Somewhat harder than kerite. Dark brown, with semi-metallic lustre. Melts before the blow-pipe to a brown glass. Decomposed by acids, with separation of scaly silica. The mean of two analyses by Chatard gave—

SiO ²	Al ² O ³	Fe ² O ³	FeO	NiO a. CoO	MgO	K ² O	Na ² O	Li ² O	H ² O
34.22	21.53	12.41	0.32	0.12	14.46	5.70	0.51	trace	11.85 = 101.12

agreeing nearly with the formula $3\text{RO} \cdot 2\text{SiO}^2 + 2(\text{R}^2\text{O}^3 \cdot \text{SiO}^2) + 5\text{H}^2\text{O}$. About one-sixth of the RO consists of alkalis, R²O. The mineral contains numerous fragments of bluish-grey corundum, and small, shining, red-brown crystals of another mineral, probably sphene.

3. *Willcoxite*.—Laminar groups resembling tale; white, greenish, or greyish-white, with nacreous lustre. Melts with difficulty to a white enamel, colouring the outer flame yellow. Dissolves in hydrochloric acid, with separation of flocculent silica. The following is the mean result of two analyses, one of a specimen from Shooting Creek, forming the crust of a corundum nucleus; the other from the Cullakence Mine, Clay Co., North Carolina.

SiO ²	Al ² O ³	Fe ² O ³	FeO	MgO	Na ² O	K ² O	Li ² O	H ² O
29.23	37.52	1.33	2.41	17.28	6.48	2.44	trace	3.66 100.35

These numbers lead to the formula $3(2\text{RO} \cdot \text{SiO}^2) + 2(2\text{R}^2\text{O}^3 \cdot \text{SiO}^2) + 2\text{H}^2\text{O}$. About one-fifth of the RO consists of alkalis, R²O.

4. *Dudleyite*, from Dudleyville, Alabama, is probably a transformation-product of margarite, which it accompanies. Colour, brown-yellow to bronze. Lustre, nacreous. Before the blowpipe it exfoliates, and melts with difficulty to a brown-yellow mass. Soluble in hydrochloric acid, with separation of flocculent silica.

SiO ²	Al ² O ³	Fe ² O ³	FeO	MgO	Li ² O	Na ² O	K ² O	H ² O
32.42	28.42	4.90	1.72	16.87	0.19	1.52	0.56	13.43

Hence the formula $2(3\text{RO} \cdot 2\text{SiO}^2 + (4\text{R}^2\text{O}^3 \cdot 3\text{SiO}^2) + 10\text{H}^2\text{O}$ (Genth, *J. pr. Chem.* [2], ix, 109).

Among the pseudomorphs and transformation-products of corundum, above enumerated, the following are deserving of special notice.

1. *Pseudomorphs of Spinel after Corundum*.—These occur in several places: (1.) In Hindostan. From this locality Genth received a number of crystals partly intergrown with orthoclase and micas, and therefore probably originating from granite. Many of these crystals exhibit distinct pyramidal forms, as well as the basal face. They are in various stages of transformation, which always takes place from without inwards, so that there is always a nucleus of corundum present. Those in which the conversion into spinel is complete have a black colour, granular texture, and semi-metallic to vitreous lustre. The streak-powder is grey, and slightly magnetic. Hardness = 8. Sp. gr. = 4.208.

(2.) On the road between Unionville and Kennett Square, Delaware Co., Pennsylvania, mixed with tale, actinolite, chlorite, and corundum, is found a black granular mineral harder than quartz, which has been recognised as spinel.

(3.) In the Calsagee mine in North Carolina, a vein of spinel occurs traversing chlorite. The spinel is partly fine- to coarse-grained, partly crystallised in the combination O. ∞ O. The crystals are often covered with a brown crust, and contain rutile in their interior; they are also associated with grains of corundum and laminae of chlorite.

(4.) Another specimen from the same locality resembles the chlorospinel from Slatoust: greenish-black octahedrons with strongly striated dodecahedral faces, accompanied by chlorite and white corundum; it frequently also contains corundum in its interior.

(5.) Another specimen from the same place shows distinctly that it was once a

corundum crystal $1\frac{1}{2}$ inch in diameter; it now consists of a nucleus of black spinel surrounded by chlorite.

(6.) In the chlorite of Dudleyville, Tallapoosa Co., Alabama, there occurs a black spinel quite surrounded by white cleavable corundum.

The specimens from Hindostan were analysed by Genth; the rest by König:—

	Hindostan	Unionville			Culsagee		
					Fine-grained	Coarse-grained	Dark green cryst.
Alumina	48.87	48.10	54.61	60.03	62.38	68.08	
Ferrie oxide	17.30	18.17	4.10	9.49	7.79	1.75	
Chromic oxide	—	—	—	3.23	1.81	—	
Ferrous oxide	23.53	23.25	10.67	9.33	11.89	11.02	
Magnesia	6.86	6.66	13.83	16.74	14.98	19.29	
Cupric oxide	—	—	—	—	—	0.11	
Nickel oxide	—	—	—	—	—	0.24	
Silica	—	—	1.26	1.14	1.56	—	
Corundum	4.31	4.31	16.24	—	—	—	
	100.87	100.49	100.71	99.96	100.41	100.49	

These analyses (disregarding mechanical admixtures) show that the pseudomorphs after corundum from Hindostan, and the dark green mineral from Culsagee are mixtures of the spinel varieties, pleonast (MgO ; FeO), (Al^2O^3 ; Fe^2O^3), and hercynite, $\text{FeO} \cdot \text{Al}_2\text{O}_3$, while the other specimens from Culsagee likewise contain the chromiferous variety called picotite. The spinel from Unionville is probably a mixture of pleonast and hercynite (Genth, *J. pr. Chem.* [2], ix. 61).

2. *Tourmalin as a transformation-product of Corundum.*—Tourmalin is well known to be one of the minerals ordinarily accompanying corundum. At Unionville, in Pennsylvania, it frequently occurs with corundum, forming irregular masses varying in size from small grains to lumps several inches in diameter, especially in laminar margarite, or with zoisite and euphyllite. It often exhibits prismatic faces, but mostly forms a granular filling between corundum. In the Culsagee mine, Alabama, is found a black tourmalin containing crystals of corundum irregularly distributed through its mass. The tourmalin is traversed by laminae of chlorite. Particles of tourmalin are often enclosed by crystals of corundum, or the contrary. In general, the tourmalin appears as matrix of the corundum. Sometimes there occurs an almost imperceptible passage of corundum into tourmalin. The upper end of one crystal of tourmalin consists of corundum, which also penetrates into the tourmalin. Very remarkable is a pseudomorph of tourmalin after corundum. It consists of a fragment of a reddish-grey corundum crystal, somewhat more than two inches in length and breadth, and exhibiting faces of the prism and pyramid. At the upper end of the crystal, nearly all the corundum is converted into black tourmalin, leaving only a shell of corundum from $\frac{1}{4}$ to $\frac{1}{2}$ inch thick; at the lower end the corundum is still an inch thick, but mixed with tourmalin. The tourmalin is traversed by laminae of chlorite (Genth, *ibid.* 75).

3. *Fibrolite and Cyanite as transformation-products of Corundum.*—At the Jantic Falls, not far from Norwich, in Connecticut, small crystals of sapphire are found completely enveloped by fibrolite, doubtless in consequence of a partial conversion of corundum into fibrolite. At Mineral Hill, Delaware, Pennsylvania, there occur in a elspathic rock, variously coloured crystals of corundum, exhibiting six-sided stars on their terminal faces, and a fibrous structure when magnified. At the part where the transformation of the corundum begins, it is covered with a thin greyish-white deposit having a glassy lustre, and a fibrous structure radiating from the corundum. Many crystals have still a nucleus of corundum, others are completely transformed, and here remain crystals having a confused fibrous structure, pseudomorphs of fibrolite after corundum. Their sp. gr. is 3.286, and their composition:—

SiO^2	Al^2O^3	Fe^2O^3	MnO	MgO	CaO	Loss by ignition
37.37	60.52	0.90	0.10	0.25	0.38	0.48

Within the serpentine region of Delaware and Pennsylvania, various fibrolite-lates are found, probably originating from corundum, especially one at Media, Pa., which exhibits a silky lustre on its fibres, encloses crystals of cyanite and staurolite,

and resembles the paragonite slates of Switzerland. Finally there occurs, amongst numerous corundum crystals, partly converted into damourite, from the Laurens district in South Carolina, a broken crystal converted on the outside into fibrolite, and having the form of a hexagonal prism $\frac{3}{8}$ inch long and $\frac{1}{4}$ inch thick with a nucleus of unaltered corundum. From the surface towards the nucleus the fibrolite exhibits a radial structure.

Cyanite is one of the ordinary accompaniments, and one of the most important transformation-products, of corundum. But whereas fibrolite, which is chemically identical with cyanite, affords true pseudomorphs after corundum, such pseudomorphs of cyanite are not known, probably because its broadly laminar structure has obliterated every trace of the original form. The greater, therefore, is the importance of specimens in which a nucleus of corundum is still perceptible. At Litchfield and Washington, in Connecticut, for example, rolled lumps of cyanite have been found enclosing corundum and diaspore. A fragment of a hexagonal prism of corundum from Swannon Gap, Buncombe Co., North Carolina, exhibits a corroded surface, and is in intimate contact with light blue cyanite and damourite which have been formed from it. A specimen from Wilkes, in North Carolina, shows bluish-grey cyanite crystals and laminar parts; corundum in small grains and fragments is distributed through the mass. At Crowders and Clubbs mountains, in Gaston Co., North Carolina, corundum is found in crystalline and massive lumps, partly deep-blue, partly greyish-blue or red. The undecomposed corundum is sometimes ferruginous, and contains rutile crystals of various size disseminated through its mass. Sometimes the corundum is also converted into compact margarite, which envelops the blue crystals; usually, however, into cyanite and damourite; and this transformation often proceeds so far that not a trace of corundum remains, nothing indeed but a scoriaceous mass, in the cavities of which occur crystals of cyanite and rutile, often coated with ferric hydrate (Genth, *ibid.* 77).

On the probable mode of formation of Corundum, see W. N. Hartley (*Chem. Soc. J.* 1876, ii. 248).

CORYNOCARPUS. The Karaka tree (*Corynocarpus levigata*) contains a poisonous bitter principle called Karakin (*q.v.*)

COSALITE. A sulphide of lead and bismuth, originally found at Cosala in the province of Sinaloa in Mexico, where it occurs imbedded in quartz. It was first analysed by Genth in 1868 (*J. pr. Chem.* lxx. 450), afterwards by Frenzel (*Jahrbuch f. Mineralogie*, 1874, 673). The mineral called 'Rezbanyite,' from Rezbanya in Hungary, described in 1858 by R. Hermann (*J. pr. Chem.* lxxv. 450) as a sulphide of copper, lead, and bismuth with lead sulphate, appears indeed from Frenzel's analyses to be identical with cosalite, the lead sulphate being doubtless a product of oxidation.

The following analyses I and II are by Genth; III and IV by Frenzel; V by Hermann:—

	I	II	III		IV		V
			<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	
Lead	33.99	37.52	38.04	38.13	31.93	32.56	36.01
Bismuth	37.48	39.06	35.46	36.35	44.48	45.01	38.38
Copper	—	—	0.85	0.86	3.49	—	4.22
Silver	2.81	2.48	1.24	1.50	0.22	—	1.93
Iron	—	—	3.09	2.82	1.18	—	—
Cobalt	4.22	2.41	—	—	—	—	—
Zinc	—	—	1.53	1.54	0.18	—	—
Sulphur	15.64	15.59	15.88	16.35	16.68	—	11.93
Arsenic	5.37	3.07	3.02	3.02	2.82	—	oxygen 7.14
	99.51	100.33	99.11	100.57	100.98		99.61

If the copper in IIIa be regarded as replacing lead, the small quantities of silver, iron, cobalt, and zinc reckoned with the bismuth, and the arsenic with the sulphur, the analyses I, II, III, and IV may be represented by the formula $Pb^2Bi^2S^3$ or $2PbS.Bi^2S^3$, which requires 41.32 per cent. lead, 42.02 bismuth, and 16.66 sulphur.

Cosalite has a metallic lustre, lead-grey colour, and somewhat darker streak. Hardness $2\frac{1}{2}$ –3; sp. gr. 6.22–6.33. Mild. Compact, with fine-grained to fibrous structure. On one specimen was found a single small imbedded crystal, prismatically elongated, and exhibiting rush-like striation. The mineral is doubtless rhombic, and

crystallises in the form of bismuth-glance, for it exhibits a tolerably perfect brachy-diagonal cleavage.

The cosalite of Rezbanya is accompanied by calcespar, zinc blende, iron pyrites, and copper pyrites, and is easily distinguished by its outward appearance from bismuth-glance, telluric silver, and telluric bismuth, with which it was formerly confounded (Frenzel, *Jahrb. f. Min.* 1874, 673).

COSMIC DUST. According to A. E. Nordenskiöld (*J. pr. Chem.* [2], ix, 356) small black particles are often found among snow which has fallen in situations where it is impossible that these particles could have come from any terrestrial source. They contain organic matter, metallic iron, nickel, cobalt, and phosphorus. Nordenskiöld supposes that they are associated with meteors, and that probably a similar extra-terrestrial origin may be assigned to the substance called *cryoconite*, which he formerly found on the Greenland glaciers. This substance is a silicate having the formula $2(\text{RO} \cdot \text{SiO}_2 + \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{H}_2\text{O})$; it also contains metallic particles (iron, nickel, and cobalt), and about 2 per cent. of organic matter.

COTO-BARK. This bark, used in South America as a substitute for quinine, occurs in commerce in short pieces from 10 to 20 mm. long, some flat, others slightly curved, and having a very powerful aroma, recalling those of cloves, pepper, and cassia; the taste is aromatic. The bark is very brittle, and, owing to the quantity of resin it contains, difficult to reduce to fragments.

According to Wittstein (*Arch. Pharm.* [3], vii, 213) it contains:—

A pale yellow *etheral oil*, lighter than water, with a strong aromatic smell, and sharp aromatic peppery taste.

An *alkaloid*, volatile and smelling of herrings; resembling trimethylamine or propylamine.

A *soft resin*, yellowish brown, of aromatic smell, and sharp taste; easily soluble in ether, chloroform, and alcohol, sparingly soluble in benzene, and scarcely at all in carbon disulphide. Its solution has an acid reaction. It dissolves in ammonia and alkalis, and is reprecipitated by acids. About one-seventh of the weight of the bark consists of this resin.

A *hard resin*, dark-brown, and brittle, without taste or smell; its alcoholic solution has a bitter taste and an acid reaction; it is insoluble in ether, benzene, chloroform, and carbon disulphide, is easily soluble in alkalis, and precipitated by acids. About one-tenth of the weight of the bark consists of this resin.

The other ordinary plant-constituents are also present, such as starch, gum, sugar, oxalic acid, tannic acid, formic, butyric and acetic acids.

According to Jobst (*N. Repert. Pharm.* xxv, 23) coto-bark also contains a crystalline principle, cotoïn, $\text{C}^{21}\text{H}^{20}\text{O}^8$, amounting to about 1.5 per cent. of the bark. This substance may be obtained by exhausting the bark with ether, evaporating the liquid to one-tenth of its volume, and mixing the residue with one-sixth of its bulk of petroleum-ether. On addition of the latter, and removal of the ethylic ether by evaporation, resinous substances are deposited, and crystals are obtained from the supernatant liquid.

The cotoïn thus obtained forms yellowish-white crystals which, under the microscope, appear as four-sided prisms; its melting point is 124° ; alkalis dissolve it with a yellow colour, and it is reprecipitated on the addition of acids. Concentrated nitric acid dissolves it in the cold with a blood-red colour. Fehling's solution is reduced by it slowly in the cold, but with great rapidity on the application of heat. With lead salts, it forms a precipitate having the composition $\text{C}^{21}\text{H}^{20}\text{O}^8 \cdot 2\text{PbH}^{10}\text{O}_2$.

Further experiments by Jobst (*Deut. Chem. Ges. Ber.* ix, 1633), and by Jobst n. Hesse (*ibid.* x, 249), have shown that the active principles of coto-bark are not always the same, some samples yielding, not cotoïn, but other bodies having similar but weaker medicinal properties. Jobst n. Hesse, by exhausting the bark with ether, obtained a brown resinous mass crystallising after some time, and consisting for the most part of three bodies, paracotoïn, oxyleucotin, and leucotin, which were separated by fractional crystallisation from hot alcohol.

Paracotoïn, $\text{C}^{19}\text{H}^{18}\text{O}^8$, forms small yellow laminae, easily soluble in chloroform, ether, and boiling alcohol, sparingly in petroleum and boiling water. The aqueous solution deposits it in nearly colourless laminae. It is neutral and tasteless; insoluble in ammonia, and nearly so in potash- and soda-ley; soluble in strong sulphuric and nitric acids, forming yellow solutions. It melts at 182° to a yellow liquid, which crystallises on cooling. At a higher temperature, it sublimes in brilliant yellow laminae. Baryta-water converts it into *paracotoïc acid*, according to the equation—



Paracotoïc acid forms an amorphous yellow powder. It is easily soluble in ether and alcohol, and is left as an amorphous residue on evaporating the latter solution.

The same acid is produced on heating paracotoïn with weak potash-ley, accompanied, however, by a small quantity of other products, amongst which is *paracoumarhydrin*, $C^8H^8O^4$, which forms delicate white laminae, melting at 85° , and dissolving easily in alcohol and ether, sparingly in water.

Oxyleucotin, $C^{21}H^{20}O^7$, forms thick, heavy, white, four-sided prisms, which melt at 133° . The fused substance solidifies in an amorphous mass on cooling. It dissolves easily in hot alcohol, chloroform, and ether, but not in water or alkalis. It is tasteless and neutral.

Leucotin, $C^{21}H^{20}O^6$, forms very delicate light white prisms, which melt at 97° , and dissolve very easily in alcohol and ether. It occurs in large quantity in coto-bark.

The alcoholic mother-liquor of the foregoing substances leaves, on evaporation, a brown resin, which gives up to very weak potash-ley the following body:—

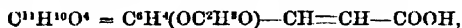
Hydrocotoïn, $C^{22}H^{20}O^4$, crystallises from alcohol in brilliant pale-yellow prisms, and from boiling water in delicate white needles. It is neutral and tasteless, melts at 98° , and solidifies to a crystalline mass. It dissolves in alkalis, and is precipitated from the solutions by acids, even by carbonic acid.

COUCH-GRASS ROOT. The root of this plant (*Triticum repens*) contains from 2.45 to 3.33 per cent. fruit-sugar, but no other kind of sugar; acid malates, but no lactates; and a gummy substance called triticein, isomeric with cane-sugar, $C^{12}H^{22}O^{11}$. This substance is prepared by precipitating the alcoholic extract of the root with basic acetate of lead, removing the lead from the filtrate, evaporating, exhausting the residue with alcohol, then dissolving it in water, repeating this treatment till the solution no longer gives a precipitate with basic lead acetate, and finally purifying the gum by dialysis. The root contains from 6 to 8 per cent. of triticein, but the quantity actually obtained does not exceed 1.5 to 2 per cent., and even this is not quite free from nitrogen.

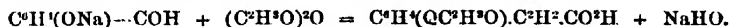
Triticein is tasteless and scentless, soluble in water, insoluble in alcohol and ether, levogyrate, with a rotation of 50° to 60.2° . The aqueous solution yields, slowly on boiling, easily under increased pressure, or on addition of an acid, a quantity of levulose corresponding exactly with the equation $C^{12}H^{22}O^{11} + H^2O = 2C^6H^{12}O^6$. Yeast does not act on triticein, but diastase quickly sets it fermenting. With sulphuric acid triticein forms a conjugated acid; with alkali-metals, compounds soluble in water; with other metals, insoluble, gelatinous, and mostly coloured compounds. By nitric acid it is converted into oxalic acid; by manganese dioxide and sulphuric acid, or by lead dioxide, into formic acid (H. Müller, *Arch. Pharm.* [3], ii. 500; iii. 1).

COUMARIC ACID, $C^9H^8O^4 = C^8H^7 \begin{matrix} \text{CH}=\text{CH}-\text{COOH} \\ \text{OH} \end{matrix}$ (Tiemann a. Herzfeld,

Deut. Chem. Ges. Ber. x. 63, 283). *Acetyl-paracoumaric acid*,



is prepared by heating a mixture of fused sodium acetate, acetic anhydride, and the sodium salt of paraoxybenzaldehyde:



The product solidifies on cooling to a radio-crystalline mass, from which water removes the sodium acetate and the excess of acetic anhydride, leaving yellow-brown acetyl-paracoumaric acid, which may be purified by sublimation or by recrystallisation from water.

Acetyl-paracoumaric acid crystallises in felted groups of white slender needles, soluble in alcohol, ether, glacial acetic acid, and boiling water, nearly insoluble in cold water, benzene, and chloroform. It melts at about 195° , and sublimes without decomposition at a lower temperature.

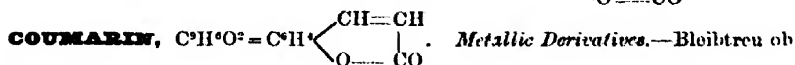
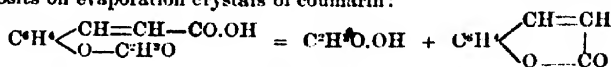
The acid heated with potash-ley is resolved into acetic and paracoumaric acid (m. p. 226°), identical with that which Hlasiwetz obtained from aloes (*Liebig's Annalen*, cxxxvi. 131) in every respect except the melting point, which Hlasiwetz found to be 180° . Tiemann a. Herzfeld have, however, prepared the pure acid from aloes, and found that it has the same melting point as the artificially prepared paracoumaric acid, viz. 226° .

Acetyl-orthocoumaric acid is obtained similarly to the para-compound, by gently heating a mixture of salicyl-aldehyde (3 pts.), acetic anhydride (5 pts.), and sodium acetate (4 pts.) for some hours. The whole then solidifies on cooling to a crystalline mass which, when treated with water, yields an oil smelling of acetic acid and coumarin; and an ethereal solution of this oil, shaken with a solution of sodium carbonate, yields thereto a crystallisable acid, whilst coumarin remains dissolved in the ether. The acid, which is acetyl-orthocoumaric acid, $C^{11}H^{10}O^4$, dissolves

easily in hot water, alcohol, and ether, and crystallises from water in white needles melting at 146° . Heated with dilute potash-ley it is resolved into acetic acid and orthocoumaric acid, $C^6H^4(OH)-CH=CH-CO^2H$, which crystallises in white needles melting with decomposition at $207^{\circ}-208^{\circ}$.

Orthocoumaric acid is converted by treatment with sodium-amalgam into hydro-orthocoumaric acid, $C^6H^4(OH)-CH^2-CH^2-CO^2H$, which crystallises in large pointed needles melting at $82^{\circ}-83^{\circ}$.

Acetyl-orthocoumaric acid, gently heated above its melting point, evolves pungent fumes of acetic acid, and ultimately leaves a thick oily body, an ethereal solution of which deposits on evaporation crystals of coumarin:



served (*Liebig's Annalen*, lix. 177) that coumarin dissolves in hot potash-ley, forming a yellow solution from which acids precipitate the coumarin unchanged. According to Perkin (*Chem. Soc. Jour.* xxii. 192), this yellow liquid is not simply a solution of coumarin in potash, but is a chemical compound of coumarin with the alkali; and by employing an excess of the former, and adding a solution of silver nitrate to the product, a yellow precipitate formed, having the composition $C^6H^4O^2.Ag^2O$, and analogous to a silver derivative obtained by Bleibtreu from nitro-coumarin, viz. $C^6H^4NO^2O^2.Ag^2O$. Perkin also mentions that the homologues of coumarin dissolve in potash, and in these instances, on boiling the solution until it is very concentrated, the alkaline derivative separates out as an oily liquid, which, on cooling, forms a tenuous mass.

A number of other metallic derivatives of coumarin have been prepared and analysed by R. Williamson (*Chem. Soc. Jour.* xxviii. 860).

Sodium compounds. The *monosodic compound*, $C^6H^4O^2.2NaHO$, is prepared by boiling a solution of 2 mols. pure sodium hydroxide for a few minutes with 1 mol. of coumarin. The resulting solution has a pale yellow colour, and, when dilute, exhibits a very marked green fluorescence. It is decomposed immediately by acids, and slowly by carbonic anhydride, the coumarin separating as a flocculent precipitate: it must not therefore be much exposed to the air.

The *disodic compound*, $C^6H^4O^2.Na^2O$, is obtained by evaporating the solution of the preceding salt, first in the exsiccator and afterwards at 100° . It then gives off water, and solidifies to a radio-crystalline mass, which becomes anhydrous at 150° , but at the same time undergoes partial decomposition. This salt is identical in composition with disodic coumarate, $C^6H^4Na^2O^2$, but it does not yield coumaric acid when treated with an acid.

The *potassium compound*, $C^6H^4O^2.2KHO$, is prepared like the sodium compound, which it resembles: it has not been obtained in the crystalline state, and like the monosodic compound it is extremely deliquescent.

The *silver compound*, $C^6H^4O^2.Ag^2O$, is obtained as a canary-yellow precipitate on adding silver nitrate to a solution of caustic soda saturated with coumarin. To obtain it pure, the precipitation must be made in the cold, and only a few drops of silver nitrate at first added, to remove any traces of free caustic soda in the product. The slight precipitate is then to be filtered off, and the precipitation completed in the filtrate. The resulting precipitate is to be well washed on a filter with cold water, and subsequently with alcohol and ether, which removes any free coumarin. It must be dried carefully, as it blackens above 100° , and sometimes below. When strongly heated it gives off coumarin, which is also liberated by treating it with nitric acid. It is very definite and uniform in composition, and appears to be permanent if kept in the dark, but gradually blackens on exposure to light.

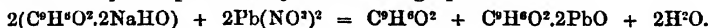
Barium compounds. A boiling solution of barium hydrate dissolves coumarin, forming a yellow liquid drying up on evaporation to a sticky mass, which stiffens on further heating and forms a brittle deliquescent substance. This product continues to give up water till heated to 200° , at which temperature it has the composition $C^6H^4O^2.BaH^2O^2$. This barium salt is similar, in properties to the alkaline derivatives of coumarin, and like them is easily decomposed by acids, and is excessively soluble in water. It has not been obtained in the crystalline state.

By heating barium hydrate and coumarin in a sealed tube to 200° for a few hours, a different barium compound is formed. The liquid in the tube becomes darker-coloured and decomposes, a bright yellow granular precipitate gradually settling down. The mother-liquor, when warmed and acidulated, gives a reddish-brown, pasty precipitate, but no coumaric acid crystallises out on cooling. This red

precipitate is insoluble in water, but is freely dissolved by hot potash and by alcohol.

The bright yellow precipitate was found to be largely mixed with barium carbonate, and it was almost insoluble in water. On treatment with acids it yielded a red amorphous powder, soluble in hot alcohol.

Lead compound. Lead nitrate or acetate, added to a solution of the sodium salt, throws down a light yellow compound accompanied by free coumarin. To obtain the yellow compound as pure as possible, it is best to precipitate in three fractions, and select the second one, which is to be washed with water, dried, pounded, and digested several times with ether till all the free coumarin is removed. The product thus obtained gives by analysis numbers agreeing nearly with the formula $C^9H^6O^2 \cdot 2PbO$. Its formation may be represented by the following equation:



The lead salt is insoluble in water, alcohol, and ether, but dissolves in an excess of lead nitrate, and falls again on stirring as a yellow granular precipitate.

Many other metallic derivatives may be formed by precipitation from a solution of the sodium salt. *Cupric sulphate* gives a yellowish-green precipitate which is somewhat soluble in excess, very unstable, and decomposed on boiling into cupric hydrate and coumarin.

Zinc sulphate forms a white gelatinous precipitate, insoluble in water. A solution of *alum* also forms a white gelatinous precipitate insoluble in water, but easily soluble in excess of the precipitant. With *ferric chloride* a chocolate-brown precipitate is produced, and with *ferrous sulphate* a precipitate of a brilliant grass-green colour.

Stannous chloride produces a bulky white precipitate.

On heating the dry sodium salt to 150° for a few hours in a sealed tube with *ethyl iodide*, a yellow liquid is formed which, when evaporated and heated to expel excess of ethyl iodide, leaves sodium iodide, together with a stiff brown oil which becomes fluid on warming, is remarkably stable, and is not apparently attacked even by boiling potash.

Acetic anhydride heated to 100° with sodium-coumarin also forms a compound, which, when separated from sodium acetate by mixing with ether and filtering, may be obtained in a gummy state by heating the filtrate, to expel the ether and excess of acetic anhydride.

Propionic Coumarin, $C^{10}H^8O^2$ (Perkin, *Chem. Soc. Jour.* xxviii. 10). This compound, intermediate between acetic (ordinary) coumarin and butyric coumarin, is formed by heating sodium-salicylal with excess of propionic anhydride, just as ordinary coumarin is formed from sodium-salicylal and acetic anhydride (1st Suppl. 500). The action must be continued at the boiling heat for an hour or more, the excess of propionic anhydride and the propionic acid formed in the reaction being afterwards distilled off. The crude propionic coumarin remaining in the retort is freed from sodium propionate by pouring it into boiling water, in which it sinks as a heavy oil, but solidifies to a brownish crystalline mass on cooling. It is collected and distilled to render it colourless, then well pressed between bibulous paper, and twice recrystallised from alcohol.

Propionic coumarin thus obtained crystallises in beautiful transparent slightly oblique prisms, smells like ordinary coumarin, melts at 90° , and solidifies to a crystalline mass on cooling; it distils without decomposition. Boiling water dissolves it to a small extent, the solution becoming milky as it cools, and afterwards depositing fine hair-like crystals. It is moderately soluble in cold, and easily soluble in boiling alcohol.

Propionic coumarin is nearly insoluble in cold aqueous potash, and when gently heated, melts and floats as an oil on the surface of the alkaline solution. If boiled, however, it dissolves, forming a clear pale yellow liquid, which becomes opaque when concentrated. On standing, an oily liquid rises to the surface, and solidifies on cooling to a tenacious mass. It is easily soluble in water, and is decomposed, with separation of the propionic coumarin, upon the addition of an acid. When fused with potash this coumarin yields a crystalline acid, probably a propionic coumaric acid, but when it is more strongly heated with potash, salicylic acid is produced.

β -Bromo-propionic Coumarin, $C^{10}H^7BrO^2 = C^9H^6 \left\{ \begin{array}{l} C^9H^6BrO \\ CO \end{array} \right.$.—If the sodium-salicylal used in the preparation of propionic coumarin be replaced by sodium-bromosalicylal, a brominated product is obtained homologous with β -bromocoumarin; that is to say, a bromopropionic coumarin having the bromine in the C^9 group:



When propionic coumarin is mixed with bromine in excess, it dissolves, and on driving off the excess of bromine and hydrobromic acid, by heating the mixture over the water-bath and then over the lamp, a crystalline product is obtained which generally weighs nearly half as much again as the coumarin employed, showing that about 1 atom of hydrogen has been replaced. On recrystallising the product from alcohol, long thin needles are obtained, which are also β -bromopropionic coumarin.

β -bromopropionic coumarin melts at 146° , and solidifies to a crystalline mass on cooling. It can be distilled with but little decomposition. It dissolves easily in boiling alcohol, but is less soluble than propionic coumarin. It dissolves gradually in boiling potash-ley, and may be precipitated unchanged by acids. When fused with potash, it gives an orange-red coloured product, together with potassium bromide.

β -Dibromopropionic Coumarin, $C^9H^7Br^2O^2 = C^9HBr^2 \begin{Bmatrix} C^8H^5O \\ CO \end{Bmatrix}$.—When propionic coumarin is heated for a few hours in a sealed tube to about 150° with twice its weight of bromine dissolved in carbon disulphide, large quantities of hydrobromic acid are formed, and on evaporating the carbon disulphide, and twice crystallising the residue from benzene, a crystalline product is obtained, the analysis of which agrees approximately with that of dibromopropionic coumarin, exhibiting, however, an excess of carbon, due probably to admixture of monobromopropionic coumarin.

This compound appears to have all its bromine in the C^9 -group, as it does not seem to be touched by caustic alkali till it is fused therewith, whereupon the mixture changes to an orange colour in the same manner as in the monobromo-derivative.

Dibromide of Propionic Coumarin.—Propionic coumarin, exposed to the action of bromine-vapour in the cold, changes to a viscid liquid, and greatly increases in weight. The product appears to be the dibromide corresponding with dibromide of coumarin, but it has not yet been obtained sufficiently pure for analysis. Caustic alkalis separate propionic coumarin from it. Dibromide of coumarin, under similar circumstances, yields α -bromocoumarin, $C^9H^7BrO \begin{Bmatrix} C^8H^5O \\ CO \end{Bmatrix}$, which, if further treated with alkalis, gives coumarilic acid.

Sulphopropionic Coumarilic Acid, $C^9H^7O^2.SO^2 = C^9H^7O^2.SO^2H$.—Propionic coumarin dissolves in fuming sulphuric acid without any change of colour, and on gently heating the mixture in the water-bath, a sulpho-acid is obtained, which is easily converted into the barium salt by treatment with barium carbonate, and filtering from the barium sulphate. On concentrating the filtrate and leaving it at rest, small but brilliant crystals are obtained, which have the composition $(C^9H^7O^2.SO^2)^2Ba + 10H^2O$, give off part of their water of crystallisation when dried in a vacuum, and the rest at 150° .

From these results it appears that, though propionic coumarin is analogous to ordinary coumarin in most of its properties, it nevertheless differs in some particulars, especially in its tendency to form β -derivatives containing the whole of the bromine in the C^9 -group, whereas with ordinary coumarin the tendency is in the opposite direction, the bromine entering most readily into the acetyl-group (see *Chem. Soc. J.* xxiv. 53).

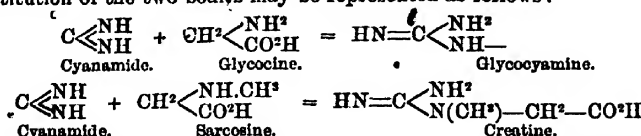
CREATINE, $C^4H^5N^3O^2$. The following tests for creatine are given by R. Engel (*Compt. rend.* lxxviii. 1707-1708): 5 or 6 drops of a 20 per cent. solution of silver nitrate are added to 2 c.c. of a cold saturated solution of creatine; and a solution of potash is then added, drop by drop, until the white precipitate which is first produced is redissolved. After a time the liquid solidifies to a transparent gelatinous mass, so that the vessel containing it may be inverted. This mass becomes reduced immediately when heated, and in the course of a few hours at the ordinary temperature.

On adding potash to a solution of creatine containing mercuric chloride, a white crystalline precipitate is produced after a time, which is insoluble in excess of the precipitant. Again, if a solution of mercuric chloride be gradually added to a solution of creatine containing potash, a white compound is first produced, and as soon as all the creatine is removed, a precipitation of the yellow mercuric oxide takes place.

The mercury-compound of creatine, $(C^4H^5N^3O^2)^2Hg.HgO$, may be obtained pure by combining creatine with mercuric oxide at a temperature between 0° and 5° ; at higher temperatures the mercuric oxide is reduced; but after the compound has been washed and partly dried in a vacuum, the drying may be completed in a current of air at 80° or 90° without risk of decomposition. The compound is white and dissolves in dilute acetic or hydrochloric acid (Engel, *ibid.* lxxx. 885).

Constitution of Creatine.—As creatine is formed by the union of cyanamide and

sarcosine (methyl glycocine) just as glycocyamine, $C^4H^7N^1O^2$, which differs from it by CH^3 , is formed by combination of cyanamide and glycocine (ii. 906; 1st Suppl. 501), it follows that creatine has the constitution of methyl-glycocyamine. The formation and constitution of the two bodies may be represented as follows:



In like manner creatinine, $C^4H^7N^2O$, is the methyl-derivative of glycocyamidine, or glycolyl-guanidine, $C^4H^5N^2O$:



Aromatic Compounds analogous to Creatine.

Benzglycocyamine, $C^9H^9N^1O^2$.—This base, related to benzoic acid in the same manner as glycocyamine to acetic acid, was first obtained by Griess in 1868 (*Deut. Chem. Ges. Ber.* i. 191) by boiling the cyanide of amidobenzoic acid with caustic potash:



afterwards by the direct union of cyanamide with amidobenzoic acid (*ibid.* vii. 574):

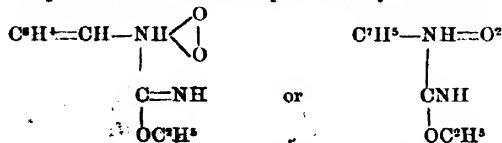


More recently it has been prepared by the action of ammonia on the basic compound $C^9H^{12}N^2O^3$, produced by the action of cyanogen on an alcoholic solution of amidobenzoic acid (1st Suppl. 318).* The reaction is:

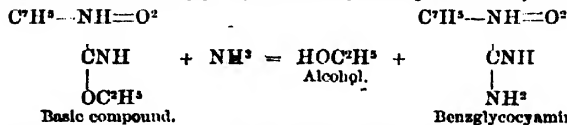


The basic compound is dissolved in cold strong aqueous ammonia, and the solution is left to itself for a considerable time. Crystals of benzglycocyamine then begin to separate after about twelve hours, but the transformation is not complete till after the lapse of several weeks. The compound may be purified by recrystallisation from boiling water (Griess, *Deut. Chem. Ges. Ber.* viii. 322).

From the results of experiments not yet published, Griess infers that the constitution of the basic compound $C^9H^{12}N^2O^3$ is represented by the formula



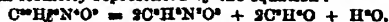
whence, if the action of the ammonia consists in the replacement of ethoxyl by amidogen, the formation of benzglycocyamine may be represented by the equation,



These compounds may also be represented by formulæ analogous to that above given for glycocyamine, viz.:



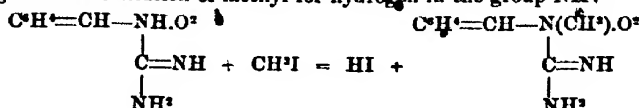
* This base was originally represented by the formula $C^9H^9N^2O^2$, which differs from the double of the new formula $C^9H^{12}N^2O^2$ only by $3H^3O$. Its conversion into uramidobenzoic acid, $C^8H^7N^2O^3$, by the action of alkalis was formerly represented by the equation:



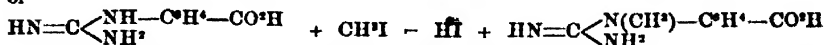
According to the new formula it is represented by the equation:



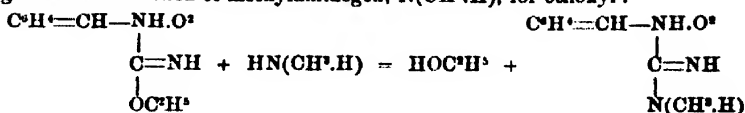
Methyl-benzglycocycamines or Benzcreatines, $C^6H^{11}N^2O^2 = C^6H^4(CH^3)N^2O^2$ (Griess, *Deut. Chem. Ges. Ber.* viii. 324). Two isomeric bodies having this composition are obtained: (a) By the action of methyl iodide on benzglycocycamine, the change consisting in the substitution of methyl for hydrogen in the group NH:



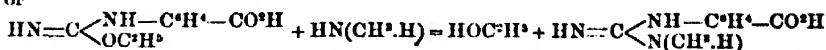
or



β . By the action of methylamine on the compound $C^6H^{11}N^2O^2$, the change consisting in the substitution of methylamidogen, $N(CH^3.H)$, for ethoxyl:



or

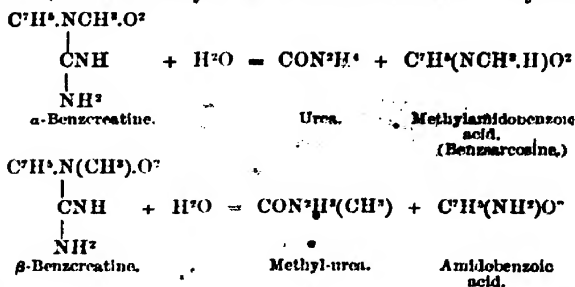


α -Benzcreatine is slightly soluble in water, from which it separates in small flat needles, containing $1\frac{1}{2} H_2O$, which can be driven off at 116° . It is very slightly soluble in alcohol or ether, and has a bitter taste. With potash, it behaves like benzglycocycamine, excepting that it dissolves only in the somewhat concentrated ley.

The hydrochloride, $C^6H^{11}N^2O^2.HCl + H_2O$, forms white rhombic leaflets easily soluble in hot water, and the platinum salt, $(C^6H^{11}N^2O^2.HCl)^2PtCl^4 + 2H_2O$, forms orange-red prisms, which are tolerably soluble in hot water.

β -Benzcreatine is moderately soluble in hot water, and separates in thin plates, which are triangular, elliptical (elongated), or hexagonal, its remaining properties being similar to those of the α -compound. The hydrochloride, $C^6H^{11}N^2O^2.HCl$, forms white prisms, which are easily soluble in water, but less soluble in hydrochloric acid. The platinum salt, $(C^6H^{11}N^2O^2.HCl)^2PtCl^4 + 2H_2O$, forms yellow, easily soluble leaflets.

α -Benzcreatine, boiled with baryta-water, splits up into methylamidobenzoic acid and urea, whereas β -benzcreatine yields amidobenzoic acid and methyl-urea:



The ureas formed in these reactions are of course not actually separated out, but are resolved, by assumption of water, the first into 1 mol. CO^2 and 2 mol. NH^2 , the second into CO^2 , NH^2 , and $NH^2(CH^3)$.

Methylamidobenzoic acid (benzsarcosine) crystallises in nodular groups of reddish leaflets moderately soluble in hot water. Its hydrochloride, $C^6H^4(NCH^3.H)O^2.HCl$, forms shining six-sided leaflets, and its aqueous solution, treated with potassium nitrite, yields white needles of nitrosomethylamidobenzoic acid, $C^6H^4(N.CH^3.NO)O^2$.

CREOSOTE and CREOSOL. The properties of English and German wood creosote have been examined by J. Williams (*Chem. Centr.* 1873, 167). English creosote, prepared from Stockholm tar, began to boil at 100° ; the thermometer rose quickly to 213° , when 6 per cent. distilled, then to 216° , when 34 per cent. passed over; 34 per cent. distilled up to 222° , and 16 per cent. up to 231° , whilst the remainder had

a much higher boiling point. German creosote from beech-wood began to boil at 200°, 40 per cent. passing over below 208°, 32 per cent. up to 210°, and 16 per cent. up to 220°; it was soluble in glycerin, whilst the English creosote was not.

According to Hofmann (*Deut. Chem. Ges. Ber.* viii. 66), the high-boiling portion of beech-wood creosote contains a liquid boiling at 279°. Treated with potassium dichromate it yields cerulignone and a compound crystallising in long yellow needles. The latter body is the oxidation-product of an oily liquid boiling at 285°, which may be obtained pure by fractional distillation and repeated recrystallisation of its sodium-salt. It has the composition $C^{11}H^{10}O^3$, and the yellow body is a quinone consisting of $C^8H^6O^4$. Reducing agents convert it into the phenol $C^8H^{10}O^4$, crystallising in white needles. Bromine changes the quinone into $C^8H^4Br^2O^4$, forming brilliant red crystals melting at 175°.

Rhenish beech-tar creosote was shown by Marasse to be separable by fractional distillation, into three portions, boiling respectively at 184°, between 200° and 203°, and between 217° and 220° (1st *Suppl.* 504). The portion boiling at 184° solidifies on cooling, and consists mainly of phenol, the fraction boiling at 200°–203°, is a mixture of guaiacol or homopyrocatechin, $C^8H^{10}O^2$, and a cresol, the methylic ether of which is converted by oxidation into anisic acid: therefore paracresol.

The third portion, boiling at about 220°, consists of phlorol, $C^8H^{10}O$, and creosol, $C^8H^{10}O^2$, together with small quantities of the substances found in the lower fractions. This portion has been further examined by Tiemann and Mendelssohn (*Deut. Chem. Ges. Ber.* viii. 1136).

The portion of the creosote boiling between 200° and 230° was dissolved in ether, and the ethereal solution shaken for some time with moderately strong potash-ley. The ethereal layer containing the neutral oils (anisolic compounds) was separated by a tap-funnel from the alkaline solution; the latter again shaken with ether to remove traces of suspended impurities, then acidulated with sulphuric acid; and the precipitated oil was dissolved up by ether. The ether was then distilled off, and the oily residue subjected to fractional distillation, whereby it was resolved into two principal portions, one boiling between 105° and 212°, the other between 217° and 226°. The former contained guaiacol and cresol; the latter creosol and phlorol.

The phlorol appears to consist of para-ethylphenol, $C^8.OH.H.H.C^2H^5.H^2$, inasmuch as a compound having the same composition and boiling at the same temperature (220°) is produced from phloretic acid, $C^8H^7 \begin{smallmatrix} OH \\ < C^2H^4(CO^2H) \end{smallmatrix}$, which, as shown by

Körner and Corbetta (*Monit. scient.* 1875, 650), is convertible, by methylation and subsequent oxidation, into anisic acid. This conclusion has not, however, been directly confirmed by experiments on the phlorol of creosote.

To determine the constitution of the creosol, the mixture of that substance and phlorol (b.p. 217°–226°) was dissolved in alcohol; the solution heated on the water-bath with a slight excess of potash till it began to crystallise; and the mass when cool was strongly pressed between bibulous paper. The crude *potassium-creosol* thus obtained was dissolved in methyl alcohol, and boiled in a reflux apparatus for two or three hours with excess of methyl iodide; the unattacked methyl iodide and the greater part of the methyl alcohol were then driven off; the residue mixed with water which separated a heavy oil; and this oil, after being several times shaken up with dilute potash to remove unaltered phenols, was subjected to fractional distillation, the greater part going over between 214° and 218°.

The compound thus isolated is nearly pure methyl-creosol, $C^8H^{12}O^2$, or dimethyl-homopyrocatechin, $C^8H^7(CH^3)2 \begin{smallmatrix} OH \\ < OCH^3 \end{smallmatrix}$. When heated with a dilute solution of potassium permanganate, it is converted into dimethylprotocatechuic acid (p. 290): consequently the creosol of wood-tar consists of methylated homopyrocatechin or homoguaiacol, $C^8H^7(CH^3) \begin{smallmatrix} OH \\ < OCH^3 \end{smallmatrix}$.

The portion of wood-tar creosote which is insoluble in potash, consists mainly of methyl-creosol.

The phenolic compounds of wood-tar creosote (soluble in potash) when mixed in alcoholic solution with *ferric chloride*, exhibit characteristic and mostly green colours, whereas the anisolic compounds (insoluble in potash unless highly concentrated), such as methyl-guaiacol and methyl-creosol, do not exhibit this coloration. This reaction serves therefore to show when the phenols have been completely converted into the corresponding ethers.

Distinction between Creosote and Phenol.—On adding an alcoholic solution of *ferric chloride* to an alcoholic solution of creosote, a dark greenish-blue colour is produced, whereas phenol similarly treated assumes only a light brown colour. By this reaction 1 part of creosote may easily be detected in 500 parts of phenol. A

small quantity of phenol in creosote cannot be detected in this manner, but its presence may be recognised by boiling a few drops of the creosote with excess of nitric acid as long as red fumes are given off, and mixing the resulting solution with potash-ley. The formation of a yellow crystalline precipitate indicates the presence of phenol, which by this treatment is converted into picric acid, whereas creosote produces nothing but oxalic acid (J. A. Clark, *Pharm. J. Trans.* [3], iii. 1037).

The presence of phenol in creosote may also be detected by heating the liquid with one-fourth of its volume of ammonia, pouring it into a large basin in such a manner as to wet the sides as much as possible, then pouring it out and holding over the basin a vessel containing bromine, so that the vapour of the bromine, as it falls, may come in contact with the drops of liquid running down the sides of the basin. The presence of phenol will then be exhibited by blue zones forming round the points of contact (Flückiger, *Arch. Pharm.* [3], iii. 30).

The following comparison of the reactions of creosote and phenol is given by A. Wätzel (*Arch. Pharm.* [3], x. 130):

	Beech-wood tar Creosote	Phenol	Maron's English Wood-tar Creosote
Ferric chloride (1 in 10)	Blue coloration, turning first brown and then orange.	Permanent violet coloration.	Blue coloration, turning olive-green and then dirty yellow.
Ferric acetate (1 in 10)	Brown coloration, with a violet tinge. Finally a brown precipitate.	Light brown colour.	Light brown colour.
Ferric sulphate (1 in 20)	Blue, with a tinge of violet, and lastly a brown precipitate.	Permanent violet coloration.	Grass-green colour, and lastly, a yellow precipitate.
Lead nitrate (1 in 10)	No change.	Cloudy, and lastly slight precipitate.	Like carbolic acid.
Zinc chloride (1 in 10)	White precipitate, soluble in excess.	Slight precipitate, insoluble in excess.	Like carbolic acid.
Lead acetate (1 in 10)	White precipitate, soluble in excess.	Slight precipitate, insoluble in excess.	White precipitate, partly soluble in excess.
When these bodies were dissolved in ten times their weight of alcohol, their reactions were—			
Aqueous ferric chloride (1 in 10).	Blue coloration, turning green.	Violet coloration, turning green.	Green coloration, turning a fine blue.
With the concentrated substances, the reactions were—			
Alcoholic ferric chloride	Dirty violet.	Yellow-green, turning brown.	Green, turning brown.

Pure guaiacol and creosol behave in the same manner as beechwood-tar creosote.

CRESOL, $C^H^3O^2 = C^H^2 \begin{smallmatrix} CH^1 \\ OH \end{smallmatrix}$. The following tabular statement of the properties of the three isomeric cresols and some of their derivatives is given by Oppenheim & Pfaff (*Deut. Chem. Ges. Ber.* viii. 888). See also 1st *Suppl.* 505; 2nd *Suppl.* 393, 391:—

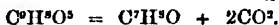
	Ortho (1 : 2)	Meta (1 : 3)	Para (1 : 4)
Cresol (1)	M. 31°-31.5° (2) B. 185°-186° (2)	M. — B. 194°-200° (2)	M. 36° B. 198° (4)
Cresotic acid	M. 163°-164° (2) B. —	M. 168°-174° (2) B. — (2)	M. 147°-150° (2) B. —
Methyl cresolate	M. — B. 174° (6)	M. — B. —	M. — B. 174° (7)
Ethyl cresolate	M. — B. —	M. — B. 188°-191° (2)	M. — B. 186°-188° (4)
Methyloxybenzoic acid	M. 98.5° (8) B. —	M. 95° (?) (6) B. —	M. 183.5°-185° B. — (10)
Ethyloxybenzoic acid	M. 19.5° (11) B. —	M. 137° (12) B. —	M. 195° (14) B. —
Oxybenzoic acid	M. 155°-156° (14) B. —	M. 200° (11) B. —	M. 210° B. —

Metacresol is formed: a. Together with carphone, C^9H^{11} , by the dry distillation of podocarpic acid or its calcium salt:



By heating the dehydrated calcium salt in short-combustion tubes, a tarry liquid is obtained, which, when distilled with small quantities of water as long as oily drops pass over, yields first a mobile liquid (carphone) lighter than water, then a thicker liquid (metacresol), heavier than water, and soluble in alkalis, while the greater part of the tar remains in the residue. The carphone and cresol are finally separated by means of potash-solution. The cresol thus obtained boils at 202°; its benzoyl-derivative melts at 68°.

b. By distillation of the barium or calcium salt of the oxyvitric acid, $C^9H^8O^2$, obtained by the action of chloroform on sodacetic ether (p. 17):



The cresol thus obtained boils at 201°; the cresotic acid obtained from it melts at 177°; the methylic ether boils at 175°-176°; the ethylic ether at 191°-192°; the corresponding methyl-oxybenzoic acid melts at 106°-107°; the ethyloxybenzoic acid at 137°; the oxybenzoic acid at 201°. These properties agree very nearly with those of the meta-cresol derivatives in the preceding table.

According to Ihle (*J. pr. Chem.* [2], xiv. 442) metacresol occurs in the crude coal-tar cresol known in commerce as 'high-boiling phenol,' or 'cresylic acid,' which also contains phenol and naphthalene. He purifies this crude liquid by dissolving it in dilute soda-ley, passing steam into the solution to remove the naphthalene, and then agitating it with baryta-water, which dissolves the phenol more readily than the cresols. By treating the mixture of cresols thus separated with sodium and carbon dioxide, he obtains two cresotic acids melting respectively at 173° and 115°-120° (p. 584), from which he infers that the cresol in question was a mixture of meta- and ortho-cresols. If so, it must be different from all the coal-tar cresols hitherto examined, which are mixtures of ortho- and para-cresol (2nd Suppl. 393, 921).

In preparing the cresols from the corresponding toluidines (1st Suppl. 506), Ihle obtained from solid para-toluidine, 50 per cent. cresol, whereas liquid ortho-toluidine yielded only 22 per cent. cresol.

Nitro- and Amido-cresols. Paracresol yields by nitration orthonitro-paracresol, $C^9.OH.NO^2.H.CH^3.H^2$,—identical with that which Wagner obtained

(1) M. signifies melting point; B. boiling point. (2) Kekulé (*Ber.* vii. 1006). (3) Engelhardt a. Latschinoff (*Bull. Soc. Chim.* [2], xlii. 256). (4) Fuchs (*ibid.* 339). (5) Biedermann a. Pike (*Ber.* vi. 323). (6) Körner (*Bull. Acad. roy. de Belgique* [2], xiv. 154). (7) Cannizzaro a. Körner (*Gazz. chim. ital.* ii. 65). (8) Graebe (*Liebig's Annalen*, cxxxix. 134). (9) Graebe a. Schuler (*ibid.* cxlii. 380). (10) Körner (*Bull. Acad. Belg.* [2], xiv. 166). (11) Oppenheim a. Pfaff (*Ber.* viii. 890). (12) Kraut (*Liebig's Annalen*, cl. 1). (13) K. A. Heints (*Ber.* ii. 497). (14) Ladenburg (*Liebig's Annalen*, cxli. 241). (15) Barth (*ibid.* cxli. 230).

from orthonitro-paratoluidine (2nd Suppl. 933)—and convertible by further treatment with nitric acid into dinitroparacresol, by bromine or iodine into monobromo- or moniodo-nitroparacresol. Potassium bromoparacresolsulphonate is converted by nitric acid into bromonitroparacresol (Armstrong a. Thorpe, *Rep. Br. Assoc.* 1875, 112).

A red powder, called 'saffron surrogate,' which is used for dyeing butter and cheese, consists of the potassium-salts of two dinitrocresols. One of them is the known compound melting at 84° (2nd Suppl. 932), and found in commerce as 'gold-yellow.' The second compound is also a dinitrocresol, which crystallises from alcohol in large yellow needles melting at 86°, and differs from the preceding by forming yellow and not red salts, resembling in that respect the dinitrocresol called 'Victoria yellow' (1st Suppl. 608), which, however, melts at 110° (Piccard, *Ber.* viii. 165; see also Wichelhaus, *ibid.* vii. 721).

By treating oxyvitric acid with fuming nitric acid, either alone or mixed with sulphuric acid, a trinitrocresol is obtained which may be purified by immersing the product in water, dissolving the separated mass in potash-ley, precipitating with hydrochloric acid, and recrystallising from alcohol. It crystallises in fan-shaped groups of smooth yellowish needles, melting at 106°. Its potassium salt has an orange-red colour and is much more soluble than the picrate. Nearly the same properties are exhibited by the trinitrocresol which Liebermann a. van Dorp obtained by heating nitrocresolic acid with water or with fuming hydrochloric acid (2nd Suppl. 367).

Dinitramidocresol, $C^6H(CH^3)(OH)(NH^2)(NO^2)^2$, is formed by the action of hydrogen sulphide on an alcoholic solution of the trinitrocresol from oxyvitric acid, and crystallises from hot water in thin, highly lustrous, amber-yellow needles; dissolves in alkalis but not in acids; melts at 156°, and decomposes at a slightly higher temperature. By passing nitrous acid into its alcoholic solution, dinitrodiazamido-dinitrocresol,



is obtained, crystallising in golden-yellow laminae which decompose at about 160° with violent explosion (Emmerling a. Oppenheim, *Ber.* ix. 1094).

CRESOLSULPHONIC ACIDS, $C^6H^3SO^3 = C^6H^3(CH^3)(OH)(SO^3H)$. On the formation of these compounds from the diazotoluenesulphonic acids, and the properties and reactions of the acids thus obtained, see 2nd Suppl. 932-934). Armstrong a. Field (*Chem. News*, xxvii. 318), by heating crude coal-tar cresol (b. p. 190°-205°) on the water-bath for several hours with an equal weight of sulphuric acid, treating the product with potash, and recrystallising, have obtained the potassium salts of three cresolsulphonic acids, the least soluble of which, crystallising with 2H₂O, is probably identical with that of Engelhardt a. Latschinoff's paracresolsulphonic acid (1st Suppl. 606). Of the two others, which are both very soluble in water, one contains 1 mol. water of crystallisation, while the other is anhydrous. By heating these potassium salts in sealed tubes with hydrochloric acid, the presence of two of the three known cresols was established, that of the third being doubtful.

The three potassium salts treated with nitric acid are easily converted into the salts of the corresponding mononitrocresolsulphonic acids, from which, by treatment with bromine, the dibromonitrocresols may be obtained. By heating the nitro-salt prepared from potassium paracresolsulphonate with nitric acid, a red dinitrocresol is obtained, which melts at 182°. From the potassium cresolsulphonate containing 1 mol. H₂O, may be obtained in like manner an isomeric dinitrocresol, melting at 85.5°, and forming characteristic potassium and silver salts of dark orange-yellow colour. The third nitrosulphonate did not yield a dinitrocresol, but by treating it with potassium nitrate and sulphuric acid, a well-crystallised potassium dinitrocresolsulphonate was obtained, convertible into bromodinitrocresol.

CRESOTIC ACIDS, $C^6H^3O^2 = C^6H^3(CH^3) \begin{smallmatrix} OH \\ COOH \end{smallmatrix}$. *Oxytoluene acids* (Ihle,

J. pr. Chem. [2], xiv. 442).—Sodium-cresol, heated in a stream of carbon dioxide, reacts like sodium-phenol, yielding cresotic acid, while half of the cresol distils over unaltered.

148°.

chloride into the alcoholic solution of this acid, is a colourless fragrant liquid may be distilled with aqueous vapour, but decomposes when distilled alone. The *methyl ether*, $C^6H^3(CH^3)(OH)(CO^2CH^3)$ obtained by boiling 1 pt. of the acid with 1 pt. sulphuric acid and 2 pts. methyl alcohol, distils undecomposed with vapour of water, and has an odour undistinguishable from that of winter-green oil.

Pure orthocresol (prepared from orthotoluidine) yields, when its very hygroscopic

sodium-compound is treated with carbon dioxide, β -cresotic acid melting at 159° – 160° . The *methylic ether* of this acid is very much like that of the α -acid.

By the action of sodium and carbon dioxide on purified coal-tar cresol (p. 582), Ihle obtained a mixture of salts, which, by fractional precipitation with hydrochloric acid, yielded first γ -cresotic acid, melting at 173.4° , acid afterwards an acid melting between 115° and 120° , which he regarded as identical with the acid (m. p. 114°) obtained by Engelhardt & Latschinoff from ortho-cresol (2nd Suppl. 394). Kekulé, however, has shown (*Deut. Chem. Ges. Ber.* vii. 1008) that the cresotic acid prepared from orthocresol melts at a much higher temperature, viz. at 163° – 164° (see Table p. 582); the lower boiling acid must therefore be one of the other ten possible modifications.

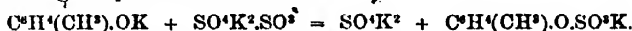
All these cresotic acids, in their external appearance, reaction with ferric chloride, solubility in chloroform, &c., are deceptively like salicylic acid; but they differ greatly from the latter in the behaviour of their potassium salts when heated; for whereas salicylic acid thus treated yields paraoxybenzoic acid (p. 285), not one of the cresotic acids is converted under similar circumstances into any acid different from itself,—except cresotic acid (m. p. 159°), which, when heated, yields two new acids not yet examined. In like manner when cresol is treated with carbon dioxide and potassium, or when potassium-cresolate is heated in a stream of carbon dioxide, the only product obtained is cresotic acid (Ihle).

Crude cresotic acid (mixture of the α , β , and γ acids) acts antiseptically like salicylic acid (Kolbe, *J. pr. Chem.* [2], xi. 9).

CRESS OILS. Garden-cress (*Lepidium sativum*) distilled with steam yields a volatile aromatic oil which does not separate spontaneously from the watery distillate, but may be extracted therefrom by agitation with benzene. Three-fourths of the crude product boiled at 226.5° , exhibited the composition of pure α -toluonitril, phenyl-acetonitril, or phenyl-methyl cyanide, $C^6H^5.CH^2.CN$, and when heated to 200° for a short time with hydrochloric acid, yielded phenyl-acetic acid. The same composition is exhibited by the volatile oil of *Tropeolum majus* (A. W. Hofmann, *Deut. Chem. Ges. Ber.* vii. 1293).

Water-cress (*Nasturtium officinale*) yields by similar treatment an oil which may be separated from the watery distillate by agitation with the most volatile portion of the so-called petroleum-ether, this solvent being afterwards evaporated off in a paraffin-bath at 140° . By fractional distillation of the remaining liquid, an oil was obtained, boiling at 253.5° (261° corr.), and having a sp. gr. of 1.0014 at 18° . This oil was found by analysis to have the composition of phenyl-propionitril, $C^6H^5.CH^2.CH^2.CN$; and on fusing it with potash, decomposing the resulting potassium salt with hydrochloric acid, and extracting with ether, phenyl-propionic acid was obtained in long needles melting at 47° (Hofmann, *ibid.* 520).

CRESSYL-SULPHURIC ACID, $C^6H^5O^4 = C^6H^5 \begin{smallmatrix} CH^2 \\ O.SO^2H \end{smallmatrix}$ (E. Baumann, *Deut. Chem. Ges. Ber.* ix. 1389, 1715). This acid, metameric with cresol-sulphonic acid (p. 583), occurs, together with phenyl-sulphuric acid, ($C^6H^5.O.SO^2H$) in the urine of the horse. Its potassium salt may be prepared synthetically (like the ethyl-sulphate) by heating a concentrated solution of potassium cresolate with potassium pyrosulphate and crystallising the product from alcohol:

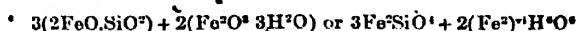


Potassium cresylsulphate is sparingly soluble in cold alcohol, more soluble in hot alcohol and in water, but less so than the phenyl-sulphate. It is coloured blue by ferric chloride when heated therewith in a sealed tube to 150° – 160° .

CRESSYL THIOCARBAMIDE, $NH^2.CS.NH(C^6H^5)$. Syn. with PARATOLYL-THIOCARBAMIDE (p. 397).

CROCIDOLITE. On pseudomorphs of quartz after crocidolite, see QUARTZ.

CRONSTEDTITE. Von Kobell, from an analysis of this mineral by Steinmann, in which he himself determined the proportions of FeO and Fe^2O^3 , deduced a formula, which, expressed in modern notation, is



The same formula has been deduced by Maskelyne & Flight (*Chem. Soc. J.* 1871, 9) from the analysis of a Cornish specimen.* It does not, however, agree very closely with either of the analyses just mentioned, as the following comparison will show:

* See 2nd Suppl. 394, where, however, the formula is misprinted.

	v. Kobell.	Maskelyne and Flight.	Theory.
SiO ² . . .	22.45	17.47	17.31
Fe ² O ³ . . .	35.35	36.76	30.77
FeO . . .	27.11	36.31	41.54
MnO . . .	2.89	—	—
MgO . . .	5.08	—	—
CaO . . .	—	0.09	—
H ² O . . .	10.70	10.09	10.38
	103.58	100.72	160.00

Maskelyne and Flight remark that the discrepancies between the quantities of the iron oxides in their analyses and the theoretical numbers may perhaps be due to an admixture of some iron hydrate, göthite for example, whose percentage of water corresponds with that of constedtite.

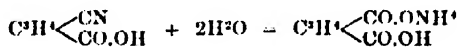
An analysis by Janovsky (*Deut. Chem. Ges. Ber.* viii. 939) of Pribram constedtite in well-defined crystals gave:—

SiO ²	Fe ² O ³	FeO	MnO	MgO	H ² O
21.30	32.34	29.23	1.25	4.51	11.90 = 100.53

whence he deduces the formula :



CROTAÇONIC ACID, C³H⁴O⁴ = C³H⁴(COOH)², (Claus a. von Wasowicz, *Deut. Chem. Ges. Ber.* x. 822). This acid, isomeric with citraconic, itaconic, and mesaconic acids, is formed, together with tricarballic acid, by the action of potassium cyanide on ethylic chlorocrotonate, which may be so conducted as to lead merely to the replacement of the chlorine-atom by cyanogen. On supersaturating the potassium salt of the resulting cyanocrotonic acid with hydrochloric acid, agitating with ether, and leaving the ether to evaporate, there remains an acid, gradually crystallising mass, which, when purified by redissolution in ether, is found to consist of ammonium crotaconate. The formation of this salt from cyanocrotonic acid is represented by the equation :

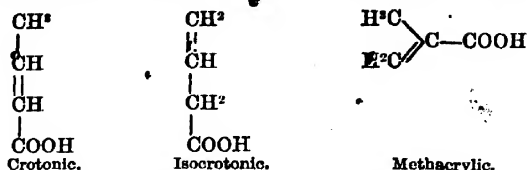


From this salt the pure acid may be obtained by supersaturation with sulphuric acid and agitation with ether. It is very soluble in water, and has hitherto been obtained only in indistinct crystals which melt at 119°. Heated above 130°, it decomposes with evolution of carbon dioxide, and production of crotonic acid. By this reaction, and by the peculiar properties of the bromopyrotartaric acid produced by addition of hydrogen bromide to crotaconic acid, the latter is shown to be a peculiar modification of the molecule, C³H⁴O⁴, distinct from the three pyrochric acids.

CROTON OIL, VOLATILE ACIDS OF. The supposition of Geuther a. Fröhlich (*2nd Suppl.* 395), that the tiglic acid which they found in croton oil is identical with Frankland a. Duppa's methyl crotonic acid (*1st Suppl.* 828), has been confirmed by the observations of Berendes (*Deut. Chem. Ges. Ber.* x. 835). Both these acids form plates having a peculiar smell like that of gum benzoin, melting at 64° and boiling at 196°–197°. The calcium salts form small, foliated, warty masses, containing 3 mols. of water; the barium salts are similar, but contain 4 mols. of water. The silver salts are white crystalline precipitates, and the two ethylic ethers boil at 154°–156°. By fusion with potash the acids are resolved into acetic acid and propionic acid. Bromine converts them into a dibromovaleric (dibromomethylethylacetic) acid melting at 82°–83°; and hydriodic acid forms moniodovaleric acid melting at 86.5°. They are not changed by the action of sodium-amalgam and water, but on heating them with hydriodic acid and phosphorus to 160°, methylethylacetic acid is formed boiling at 173°–175°, and yielding an amorphous barium salt.

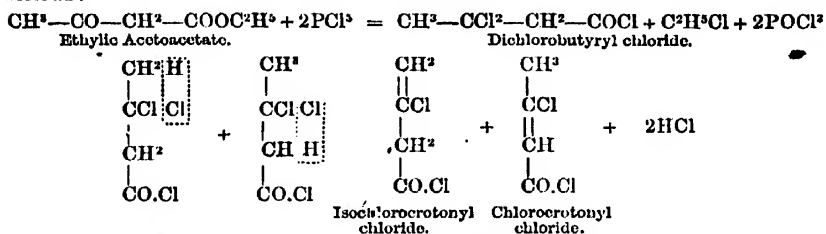
The higher-boiling portion of the volatile acids of croton oil contains small quantities of higher homologues, one of which, C⁶H¹⁰O², boiling at 204°, was isolated. Of volatile fatty acids the following were found: formic, acetic, isobutyric, and common valerician (isopropylacetic). The calcium salt of the latter forms with calcium tiglate a molecular compound crystallising in long needles.

CROTONIC ACID, $C^4H^5O_2$. There are three possible modifications of this acid, viz.:



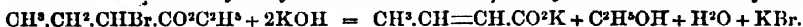
The existence of the first and third is well established; but that of the second (Geuther's *quartenylic acid*), formed by reduction of the more volatile of the two monochlorocrotonic acids produced by the action of phosphorus pentachloride on ethyl-diacetic acid (2nd Suppl. 399) has been doubted, on the ground that when heated with potash, it should yield formic and propionic acids, whereas, according to Geuther, it yields nothing but acetic acid, and therefore should be identical with solid crotonic acid. This discrepancy has, however, been removed by the observations of Hemilian (*Liebig's Annalen*, clxxiv. 322), from which it appears that isocrotonic acid is converted by heat into solid crotonic acid. This transformation takes place partially indeed every time that the liquid acid is distilled, and completely when it is heated for a quarter of an hour in a sealed tube to 170° – 180° .

The simultaneous formation of the two monochlorocrotonic acids by the action of PCl^5 on ethylic aceto-acetate (ethyl-diacetic acid) is represented by Hemilian as follows:



The dotted lines indicate the two molecules of HCl eliminated.

A confirmation of the symmetrical formula $CH^3-CH=CH-CO^2H$ for solid crotonic acid is afforded by its synthetical formation from ethylic α -monobromobutyrate:



On dropping this ether into a warm alcoholic solution of potash, a crotonic acid is obtained, yielding, between 175° and 180° , a distillate which, after repeated fractionation, boils at 180° – 182° , and solidifies in the cold. The crystals purified by pressure, two crystallisations from water, and drying over sulphuric acid, melt at 71° – 72° , and the lead salt crystallises by spontaneous evaporation in stellate groups of shining needles, as observed by Claus (1st Suppl. 510). In addition to the crotonic acid there is formed in this reaction a small quantity of an oily non-solidifying acid, which boils at 212° – 220° , and appears to consist of α -ethyloxybutyric acid, $CH^3.CH^2.CH(OC^2H^5).CO^2H$ (Hell a. Lauber, *Deut. Chem. Ges. Ber.* vii. 560).

The correctness of the symmetrical formula for solid crotonic acid is further confirmed by the fact that it is capable of being converted into butyric derivatives both of the α and the β series, viz.:



whereas an acid of the constitution, $CH^3=CH-CH^2-CO^2H$, could yield only β -derivatives, and γ -derivatives of the form $CH^3R-CH^2-CH^2-CO^2H$, but no α -derivatives.

When crotonic acid is heated on a water-bath with fuming *hydriodic acid*, it melts to a yellow liquid, which on cooling deposits large rhombic crystals of iodobutyric acid. These, when boiled with potash, are converted into oxybutyric acid; and on converting this acid into a zinc salt, and gradually adding alcohol to the solution, the zinc salt of α -oxybutyric acid, $(C^4H^7O^2)^2Zn + 2H^2O$, crystallises out first, and the last mother-liquors yield the β -oxybutyrate, $(C^4H^7O^2)^2Zn$, as an amorphous varnish. In like manner, by treating crotonic acid with hydrobromic acid, a mixture of α - and β -bromobutyric acids is obtained, which, by boiling with ammonium sulphate, are converted into the corresponding sulphobutyric acids (Hemilian, *loc. cit.*)

According to Alberti (*Deut. Chem. Ges. Ber.* ix. 1194), both crotonic and isocrotonic acid dissolve very quickly in fuming hydriodic or hydriodic acid, and the solution, after standing for some hours at ordinary temperatures, or at 0° , deposits substituted butyric acids. Crotonic acid yields with hydriodic acid, as found by Hemilian, two isomeric iodobutyric acids, one of which forms fine crystals melting at 110° ; and with hydrobromic acid, permanently liquid products. Isocrotonic acid yields liquid products with both the haloid acids. The formation of oxybutyric acids by the action of alkalis on the addition-products of crotonic acid is seldom complete, because these addition-products are to a great extent reconverted into crotonic acid even by boiling with water. The product formed by addition of HBr to isocrotonic acid yields, when treated in the manner described by Hemilian, a well crystallised zinc salt of crotonic acid, $(C^4H^5O^2)^2Zn + 2H^2O$, but no oxybutyrate. The transformation of isocrotonic acid into crotonic acid is also affected by the action of heat alone, as observed by Hemilian, but it is never complete. By the action of *sodium-amalgam* the addition-products of crotonic and isocrotonic acid are easily and completely converted into normal butyric acid, whereas the crotonic acids themselves are not altered by sodium-amalgam, even when heated with it on the water-bath for several days.

Crotonic Acid from Citraconic and Mesaconic Acids. Citraconic anhydride heated to 100° with hydrochloric acid saturated at 0° , is partially converted into citrachloropyrotartaric acid, which is resolved by boiling with strong soda-ley into an acid having the composition of crotonic acid. The product crystallises from water, in which it is easily soluble, in long, colourless prisms, which melt at 16° . It has a strong but not unpleasant odour, dissolves in all proportions of alcohol and ether, and boils constantly at 160.6° .

The *calcium salt*, $(C^4H^5O^2)^2Ca$, crystallises in tufts of long colourless needles, easily soluble in water.

The *silver salt*, $C^4H^5O^2Ag$, precipitated by silver nitrate from the calcium salt, crystallises from boiling water in long needles or in small compact crystals, which are scarcely affected by light. It dissolves sparingly in cold, and more freely in hot water. The dry salt does not lose weight at 70° , but about 100° a sudden decomposition takes place throughout the mass, the odour of the acid being evolved.

The acid is completely decomposed by melting potash at a comparatively low temperature, being resolved into propionic acid and carbon dioxide.

Mesaconic acid heated to 140° with strong hydrochloric acid, is converted into mesachloropyrotartaric acid; and the latter, by boiling with soda-ley, yields a crotonic acid identical with that obtained from citraconic acid (*Rehn, Liebigs Annalen*, clxxxviii. 42).

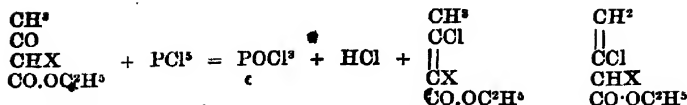
The crotonic acid thus obtained agrees with Frankland and Duppa's methacrylic acid (*1st Suppl.* 825) in its mode of decomposition by fusion with potash, but appears to differ from it greatly in physical properties, methacrylic acid being described, by its discoverers as an oily liquid not solidifying at 0° . L. Paul, however (*Annalen*, clxxxviii. 52), who has prepared methacrylic acid by a slight modification of Frankland and Duppa's process,* and obtained it in larger quantity, finds that it agrees in melting point, boiling point, and indeed in every respect, with the crotonic acid obtained from citraconic or mesaconic acid. There are, therefore, only three modifications of crotonic acid, as indicated by theory.

Methacrylic acid is completely converted into isobutyric acid by the action of *sodium-amalgam* at the ordinary temperature. This fact agrees with the observation of Geromont and Swarts (*Deut. Chem. Ges. Ber.* v. 492), that Kekulé's monobromocrotonic acid obtained from citradibromopyrotartaric acid is converted by the action of *sodium-amalgam* into isobutyric acid.

Methacrylic acid dissolves in concentrated *hydriodic acid* at the ordinary temperature, forming a clear solution. When the hydriodic acid is in large excess, the solution deposits, after some time, tufts of long prisms consisting of iodisobutyric acid, $C^4H^7IO^2$ (Paul).

βd Derivatives of the Homologues of Crotonic Acid (Demarçay, *Compt. rend.* lxxxi. 1087). These acids, or rather their ethers,—and the corresponding derivatives of other acids of the *acrylic series*—are formed by the action of phosphorus pentachloride on substituted aceto-acetic ethers (β. 12), the general equation of the reaction being $[X = CH^2, C^2H^3, \&c.]$:

* Frankland and Duppa prepared methacrylic acid by the action of PCl_5 on the ethylic ether of dimethoxallic acid, obtained by heating a mixture of ethyl oxalate and methyl iodide with amalgamated zinc, and decomposing the product with water. This process, however, is tedious, and yields but a small product. Paul finds that it is much more advantageous to start from the oxyisobutyric acid, $C(CH_3)OH.CO^2H$ (identical with dimethoxallic acid) obtained by brominating isobutyric acid, and replacing the Br by OH (*1st Suppl.* 891; *2nd Suppl.* 884).



On adding the phosphoric chloride, effervescence takes place, and on gently heating the mixture for some time, a red colour is produced, due to the reaction of POCl^3 on the substituted aceto-acetic ether.

When the action is complete, water is added to decompose the oxychloride, a heavy oil being then precipitated, which is the ether of the chlorinated acid mixed with traces of the free acid. The supernatant water also contains a certain portion of this acid, which may be extracted by ether. The main bulk of the chlorinated acid is obtained by saponifying its ether with alcoholic potash, expelling the alcohol from the aqueous solution of the resulting potassium salt by heating it in the water-bath, and decomposing this salt with hydrochloric acid. A brown oil then separates, consisting of the impure acid, which may be purified by distillation with steam.

Chloromethylcrotonic acid, $\text{C}^3\text{H}^3\text{ClO}^2 = \text{CH}^3 - \text{CCl} = \text{C}(\text{OH}^3) - \text{CO}^2\text{H}$, obtained in this manner from ethylic methyl-acetoacetate, crystallises on distillation in the cooled receiver. Towards the end of the distillation a few drops of an oily acid are obtained, probably an isomeric modification of the acid. The solid acid melts at 67° , and boils at $209^\circ - 210^\circ$. It is moderately soluble in boiling water, and crystallises therefrom on cooling in thin laminae, often 4 or 5 centimeters long. Its ethylic ether boils at $177^\circ - 180^\circ$. The acid, gently heated with strong sulphuric acid, is decomposed, with evolution of hydrochloric acid and formation of a sulpho-acid, the barium salt of which decomposes when its aqueous solution is boiled, with evolution of carbon dioxide and formation of an uncrystallisable barium salt of a new sulpho-acid. Chloromethylcrotonic acid is slowly attacked by bromine at $60^\circ - 70^\circ$, giving off hydrobromic acid. Heated to 140° with excess of potash or ammonia, it is completely resolved into carbon dioxide and chlorobutylene, $\text{C}^3\text{H}^3\text{Cl}$, the decomposition beginning even at 100° .

Chlorethylcrotonic acid, $\text{C}^3\text{H}^3\text{ClO}^2 = \text{CH}^3 - \text{CCl} = \text{C}(\text{C}^2\text{H}^5) - \text{CO}^2\text{H}$, prepared from ethylic ethylacetoacetate, melts at $74^\circ - 75^\circ$, and is partly decomposed by boiling. In purifying it by distillation with aqueous vapour, a small quantity of an oily modification is formed, as in the case of the preceding acid. At 170° it decomposes with effervescence, and yields on distillation a neutral body which smells like chlorobutylene and readily unites with bromine. This body is probably chloramylene: $\text{C}^3\text{H}^3\text{Cl} = \text{C}^3\text{H}^3\text{ClO}^2 - \text{CO}^2$. The distillate also contains a liquid acid. Chlorethylcrotonic acid is easily attacked by bromine, giving off hydrogen bromide.

Chlorowinyl-dimethylacetic acid, metameric with the acid last described, is obtained from ethylic dimethylacetoacetate. It is purified by distillation with steam, and forms monoclinic crystals which melt at $63^\circ - 64^\circ$, and decompose at 100° .

Chlorisopropylcrotonic acid, $\text{C}^3\text{H}^3\text{ClO}^2 = \text{C}^3\text{H}^3[\text{CH}(\text{CH}^3)]\text{ClO}^2$, is at ordinary temperatures a viscid oil having a faint odour. It crystallises at -25° , and decomposes on distillation, yielding products apparently analogous to those obtained from chlorethylcrotonic acid.

Chloropropylcrotonic acid is a mobile oil having a repulsive odour, decomposing on distillation, and solidifying in a freezing mixture at -28° . It is easily attacked by bromine, with evolution of hydrogen bromide.

CROTONIC CHLORAL. The compound, formerly designated by this name, and represented by the formula $\text{C}^4\text{H}^4\text{ClO}$ (2nd Suppl. 401), has been shown, by the recent experiments of Pinner, to consist of butyric chloral, $\text{C}^4\text{H}^4\text{ClO}$ (pp. 50, 443).

CROTONYL BROMIDE, $\text{C}^3\text{H}^3\text{Br}$, obtained by the action of alcoholic potash on isobutylene bromide, $(\text{C}^3\text{H}^3\text{Br}^2 - \text{HBr} = \text{C}^3\text{H}^3\text{Br})$, is a liquid boiling at 90° . It is not acted upon by alcoholic ammonia except in the nascent state. (See the next Article).

CROTONYLAMINES, $\text{C}^3\text{H}^3 \cdot \text{NH}^2$, &c. (A. W. Hofmann, *Deut. Chem. Ges. Ber.* vii. 514). These bases are formed, together with butylene-diamines, by heating isobutylene dibromide (b. p. $148^\circ - 149^\circ$) to 100° with alcoholic ammonia, part of this dibromide being resolved into HBr and crotonyl bromide, and this latter being converted by the ammonia into crotonylamines. The mixture of bases remaining after treating the product of the reaction with alkali, boiled between 80° and 300° . As these bases could not be separated by fractional distillation, an attempt was made to determine their nature by converting them into thiocarbimides. For this purpose the mixture was distilled, and a sample taken from time to time was boiled with alcohol and carbon disulphide, the alcohol evaporated, and the residue heated with solution of mercuric chloride. The portions boiling above 120° yielded no thiocarbimides, but the lower-boiling portions yielded a thiocarbimide in the form of a colourless liquid

boiling at about 170° and having a pungent odour like that of ordinary mustard-oil (allyl-thiocarbimide), but decidedly different from that of secondary butylthiocarbimide (scurvy-grass oil). Crotonyl-thiocarbimide, treated with strong ammonia, solidifies to a well-crystallised thiocarbamide (crotonyl-thiosinamine) melting at 85° (allyl-thiosinamine melts at 70°).

CROTONYLENE, $C^4H^2 = HC \equiv C - CH^2 - CH^2$, *Ethylacetylene* (2nd Suppl. 401).—This hydrocarbon occurs amongst the products obtained by the compression of coal-gas. It boils at 20° – 25° , and forms a tetrabromide which melts at 115° – 116° , and crystallises in shining needles (Caventou, *Bull. Soc. Chim.* xx. 72). A hydrocarbon, probably identical with this, has been obtained by Henninger (*ibid.* xix. 145) by distilling erythrite with five times its weight of concentrated formic acid. Reduction then takes place towards 230° , the form of glycol, $C^4H^4(OH)^2$, passing over and carbon dioxide being given off, together with the hydrocarbon C^4H^2 . This latter condenses in a freezing mixture to a limpid liquid, and unites rapidly with bromine, forming the compound $C^4H^2Br^4$, which crystallises in white flattened needles or rhombic laminae with two truncated summits, melts at 116° , and easily sublimes. Crotonylene is also found amongst the hydrocarbons obtained by passing the vapours of low-boiling petroleum through a red-hot tube (2nd Suppl. 401), and among those which are formed by the decomposition in an atmosphere of nitrogen of the solid condensation-product of acetylene produced under the influence of the dark discharge (p. 34) (Berthelot, *Compt. rend.* lxxxii. 1283).

A hydrocarbon isomeric with crotonylene has been found in small quantity, together with amylene, hexylene, benzene, and carbon disulphide, in the first runnings of the distillation of crude benzene. The tetrabromide obtained from it boiled at 99° , and gradually decomposed, with separation of hydrobromic acid (Helbing, *Liebigs Annalen*, clxxii. 281).

• **CRYTOCONITE**. The name is applied by Nordenskjöld (*Pogg. Ann.* cli. 154) to a grey lumpy powder which he collected in 1870 on the ice in the interior of Greenland. This powder covers the ice in some places to the depth of several millimeters, and is heaped up here and there in large quantities by the streams which traverse the glacier. The microscope shows a few yellow cleavage fragments (folspar?), green crystal fragments (augite?), and a small quantity of magnetic iron ore; whilst the main bulk of the powder consists of colourless, angular, transparent grains. An analysis by G. Lindström gave:

	SiO ²	Al ² O ³	Fe ² O ³	FeO	MnO	CaO	MgO
	62.25	14.93	0.74	4.64	0.07	5.09	3.00
	K ² O	Na ² O	P ² O ⁵	Cl	X*	H ² O†	Total
	2.02	4.01	0.11	0.06	2.86	0.34	100.12
							Sp. gr. 2.63 at 21°

* Water and organic matter, given off above 100° .

† Given off between 73° and 140° .

Nordenskjöld himself found in this dust metallic iron, together with cobalt, copper, and nickel, and is therefore inclined, notwithstanding its great resemblance to a volcanic ash, to assign to it an extra-terrestrial origin.

A cosmic origin is likewise attributed by Nordenskjöld to the blackish dust which occurs mixed with snow in several localities in Sweden, Finland, and Spitzbergen. This dust also contains metallic iron, and its occurrence in an ice-field in the northern part of Spitzbergen is regarded by Nordenskjöld as completely excluding the idea of a terrestrial origin of the iron. Phosphorus, cobalt, and perhaps nickel, were also found in it, and the residue insoluble in acids contained fragments of diatoms.

CRYOHYDRATES. See HYDRATES.

See GLASS.

CRYPTOMORPHITE, also called *Pricrite* (Chase & Silliman, *Sill. Am. J.* [3], v. 287). A hydrated calcium borate, from Curry County, Oregon, where it occurs sometimes in the form of veins in a slate, sometimes in layers of concretions. Under the microscope rhombic crystals may be recognised.

A. The harder variety, forming the veins. B. The softer variety, forming the concretions; analysed by Th. Price. C to E. Analyses of the latter variety by H. Silliman, who refers them to the formula $3CaO.4B^2O^3 + 6H^2O$ (F.)

	BO ²	CaO	NaCl	Fe ² O ³	Al ² O ³	H ² O	Total	Sp. gr.
A.	45.20	29.80	trace	—	—	25.00	= 100	—
B.	47.04	29.96	0.25	—	—	22.75	= 100	—
C.	48.50	32.38		0.93		18.29	= 100.10	} 2.262–2.298
D.	49.34	31.37		1.60		16.29	= 100	
E.	50.01	31.73		0.97		18.29	= 101	
F.	50.36	30.21		—		19.43	= 100	

* Estimated by difference.

CRYSTALLISATION. The formation of crystals in a liquid cooled to its point of solidification, and in a saline solution cooled below its point of saturation, is explained as follows by de Coppet (*Ann. Chim. Phys.* [6], vi. 275), on the principles of the mechanical theory of heat. If the liquid contains a crystal of the substance of salt, the liquid molecules of sufficiently low temperature—that is, those whose motion is sufficiently slow—which encounter the already formed crystal, easily fix themselves on its surface. But if there be no crystal already formed, then the formation of the first crystalline element requires the simultaneous encounter of several liquid molecules in certain states of motion. This encounter being, so to speak, accidental, may not occur for a long time, or not at all; but as the temperature is lowered, the number of molecules in the suitable condition increases. In the saline solution, the chances of the encounter of a sufficient number of molecules are diminished by the interposition of the molecules of the solvent, and by the modifications of the atomic grouping, which may be induced by its chemical action on the dissolved substance. It follows—1. That the time required for spontaneous crystallisation should be shorter as the temperature is lower, and in the case of supersaturated solutions, as the liquid is more concentrated; and 2. That the time should, in general, be inversely as the mass of the fused body or supersaturated solution. The first deduction is fully confirmed by experiment, but the second has not yet been rigorously verified.

On the Symmetrical Growth of Circularly Polarising Crystals, see Groth (*Pogg. Ann.* clviii. 214; *Jahrb. f. Min.* 1876, 602; *Chem. Soc. Jour.* 1877. ii. 116).

Unequal Solubility of different Faces of the same Crystal.—Pfaundler explains the phenomena of a crystal changing its shape without alteration of weight in a saturated solution of the same substance at a constant temperature, by supposing that when the molecules of the liquid come in contact with the crystal molecules, they may either be reflected, they may adhere, or they may tear away some of the latter. As the crystal does not alter in weight, it follows that as many molecules adhere as are torn away, and if the average energy of vibration were the same on all the surfaces of the crystal, and in all directions, the crystal would not alter in form. If, however, it is not equal on all the surfaces, some will present less resistance to the molecular action and will decrease, whilst the others, at which it is greater, will increase, and thus the crystalline form will be altered without any change of weight (*Chem. Centr.* 1875, 498).

See also Lecoq de Boisbaudran (*Compt. rend.* lxxx. 1007; *Chem. Soc. Jour.* 1875, 729).

On the Inequality of Action of Isomorphous Bodies on the same Solution, see Lecoq de Boisbaudran (*loc. cit.*)

Structure of Isomorphous Crystals.—Rammelsberg (*Deut. Chem. Ges. Ber.* ii. 31) considers that the molecule of a crystal consists of a group of single molecules, and Kekulé (*ibid.* 32) infers, from the isomorphism of certain ferrous salts with magnesium or calcium salts, that a like crystalline form does not necessarily imply a similarity of the molecules on all sides, but may be a consequence of partial similarity, and perhaps even of similarity on one side only of the molecules.

Certain observations made by Baumhauer (*ibid.* v. 867) on the form of the corrosion-figures produced by the action of solvents on various isomorphous crystals appear to favour this latter view. These corrosion-figures are mostly microscopic hollows bounded by regular surfaces, the form of which evidently bears a certain relation to the general proportions of symmetry of the crystal. The figures produced on isomorphous crystals always exhibit a certain similarity of form, but have not always the same position relative to the surfaces of the crystal. Thus there is no important difference between the figures produced by water with the isomorphous members of the monoclinic group, sulphate of iron, sulphate of iron and ammonium, sulphate of nickel and potassium, and sulphate of nickel and ammonium. The figures correspond in position, although the analogous surfaces of these bodies do not behave in exactly the same manner (which is in accordance with the slight differences of angle existing between them). In particular the figures on the two latter salts resemble each other very closely.

The group calc spar, dolomite, and spathic iron ore exhibits a contrary behaviour. Hydrochloric acid produces on the rhombohedral cleavage-planes of calc spar hollows of the form of an isosceles triangle, with the apex towards the terminal summit of the crystal. Similar figures are produced by hydrochloric acid on the rhombohedral cleavage-planes of spathic iron ore, but in this case the base of the triangular hollow is towards the terminal summit of the crystal. According to Haushofer, dolomite behaves similarly to spathic iron ore.

The close resemblance or the difference in the position of the corrosion-figures in these isomorphous bodies would appear to point to a resemblance or difference in the structure or molecular form of the crystals.

On the Corrosion-figures of Crystals, see also Exner (*Pogg. Ann.* cliii. 53; *Jahres*¹).

f. Chem. 1874, 6; H. Baumhauer, *Pogg. Ann.* cliii. 75, 621; *Jahresb.* 1875, 6; *Jahrb. f. Mineralogie*, 1876, 602; *Chem. Soc. J.* 1877, ii. 115; Sohneke (*Pogg. Ann.* clix. 329; *Jahresb.* 1876, 3).

Influence of Crystallisation-water on Crystalline Form.—According to A. E. Nordenskiöld (*Deut. Chem. Ges. Ber.* vii. 475) this influence is much less than is generally supposed. A distinction must be made, in the first place, between *isomorphous* bodies, which agree in atomic constitution, and belong to the same crystalline system, with the same or nearly the same axial constants, and *homœomorphous* bodies, which agree in chemical composition and in fundamental shape and axial constants, but crystallise in different systems.

The felspars, for instance, and the several varieties of augite, &c., form homœomorphous groups; calcspar is isomorphous with spathic iron ore, homœomorphous with arragonite, witherite, &c.

In many bodies a distinction must be drawn between the 'nucleus constituent' (Kernbestandtheil) and the 'addition constituent,' which latter has little influence on the crystalline form.

In the felspar group, anorthite is the nucleus constituent, silicic acid the addition constituent:—

Anorthite, $(R^{\cdot}R^{\cdot})O.SiO^2 + R^2O^{\cdot}.SiO^2$		
Labradorite	"	+ SiO^2
Andesite	"	+ $2SiO^2$
Oligoclase	"	+ $2\frac{1}{2}SiO^2$
Albite	"	+ $4SiO^2$
Orthoclase	"	+ $4SiO^2$

The different varieties of staurolite are compounds of the common nucleus $RO.ASiO^2 + R^2O^{\cdot}.SiO^2$, with 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, or 4 SiO^2 , &c.

Compounds containing water of crystallisation are only particular, but still important cases of this kind of combination. Hence, without reference to the amount of addition- or crystallisation-water, those crystals which have the same nucleus-constituent are, as a rule, homœomorphous.

On Crystal Crusts or Shells, see Zerrenher (*Jahrb. f. Mineralogie*, 1875, 652; *Chem. Soc. J.* 1876, i. 51).

On the Determination of the Elasticity of Regular Crystals in different directions, see P. Groth (*Jahrb. f. Min.* 1876, 199; *Chem. Soc. J.* 1876, ii. 42).

On the Pyro-electric Properties of Symmetric Crystals, see W. Hankel (*Pogg. Ann.* cliii. 161).

This mineral, first obtained from Cuba, and examined by Breithaupt, has lately been discovered in two Swedish mines, namely, those of Tunaberg and Käfveitorp. Three analyses agreed with the recognised formula $\begin{matrix} 2FeS \\ CuS \end{matrix} \cdot FeS^{\cdot}$ (Cleve, *Jahrb. f. Mineralogie*, 1873, p. 90).

E. A. Schmidt (*Arch. Pharm.* [2], exci. 1) obtained by distillation of cubebs, 14 per cent. of volatile oil. Old cubebs yielded oil separable by fractionation into two others, of sp. gr. 0.929 and 0.937 respectively; the lower specific gravity was likewise exhibited by the oil distilled from the stalks of cubebs. The lighter oil boils at 220°, the heavier at 250°. Both are laevogyrate, and have the composition $C^{15}H^{21}$. From the oil of old cubebs (but not from that of the stalks) a camphor, $C^{15}H^{25}O$, was obtained, apparently formed from the light oil. By boiling pulverised cubebs with water, Schmidt obtained a substance which he called *muos*, having the composition $C^{15}H^{16}O^{\cdot}$. Cubebin, the crystalline substance obtained by exhausting with alcohol the pulpy residue left after the preparation of the volatile oil (ii. 171), has, according to Schmidt, the composition $C^{22}H^{34}O^{\cdot}$; it does not exhibit the characters of a glucoside. The acid resin, called by Bernatzik cubebic acid (2nd Suppl. 402), Schmidt finds to be a bibasic acid, $C^{18}H^{14}O^{\cdot}$. He has also obtained from cubebs an indifferent resin having the composition $C^{12}H^{14}O^{\cdot}$.

Schaer s. Wyss (*Arch. Pharm.* [3], vi. 316) confirm Schmidt's statements as to the composition and properties of cubebs-camphor, and find that it melts at 67°. The camphor they examined (5 or 6 grams) had separated from oil of cubebs (25 grams) which had been kept for several years, in large apparently rhombic crystals. Oil prepared from old cubebs did not deposit any camphor when exposed to a low temperature, even when continued for several weeks.

The constituents of cubebs have also been examined by A. Ogliarolo (*Gazz. chim. ital.* v. 467). Cubebs distilled in a current of steam yielded about 4 per cent. of a

volatile oil, from which, after rectification and drying over calcium chloride, a small quantity of a terpene, $C^{10}H^{16}$, was obtained, boiling at 158° – 168° , together with a considerable quantity of oil boiling at 250° – 270° , evidently a mixture, but no traces of the oil boiling at 220° observed by Schmidt.

When the portion boiling at 250° – 270° was mixed with half its weight of ether and saturated with hydrochloric acid, a crystalline hydrochloride, $C^{10}H^{24}.HCl$, was separated, whilst the mother-liquor, after evaporation of the ether, and separation of a further portion of the hydrochloride which crystallised out, was washed with dilute alkali, dried, and submitted to fractional distillation. The greater portion passed over at 262° – 267° , and exhibited a slight laevorotatory power, although it is doubtful whether this power is inherent in the last-mentioned hydrocarbon, or is due to the admixture of a small amount of that which forms the crystalline hydrochloride. The hydrochloride crystallises from boiling alcohol in long colourless needles, melting at 117° – 118° , and when heated for some time to 170° – 180° with water in sealed tubes, is completely decomposed into hydrochloric acid and a hydrocarbon of the formula $C^{10}H^{24}$. This, after purification by rectification from sodium, has a density of 0.9289 at 0° , and boils at 264° – 265° . In a tube 10 centimeters long it deflects the polarised ray $44^{\circ}50$ degrees ($160^{\circ} 12'$) to the left. The hydrochloride also has a considerable action on polarised light.

CULSAGEITE. See VERMICULITES.

CUMARRYDRIN. A constituent of Coto-bark (p. 573).

CUMENE, $C^9H^{12} = C^9H^5.CH(CH^3)^2$. *Isopropylbenzene*. — This hydrocarbon, which exists ready-formed in Roman cumin oil, and is produced by distilling cumic acid with lime or baryta (1st Suppl. ii. 173, 294), may also be formed synthetically by the action of sodium on bromobenzene and isopropyl iodide. The sodium is added to the isopropyl iodide, and a solution of the equivalent quantity of bromobenzene in six times its volume of anhydrous ether is poured upon the mixture. A slow action then takes place, and after it has gone on four days, the mixture may be heated for a few hours to the boiling point, and the cumene separated by fractional distillation. The yield is but small. The cumene obtained by this process was identified with the hydrocarbon prepared from cumic acid by converting it into the sulphonic acid, and comparing the strontium and barium salts of that acid with those of the sulphonic acid prepared from ordinary cumene (Jacobsen, *Deut. Chem. Ges. Ber.* viii. 1260).

Cumene treated with chlorine in presence of iodine, and afterwards heated to 200° with iodine trichloride in sealed tubes, is converted into perchloromethane and perchlorobenzene:



(Krafft a. Merz, *Deut. Chem. Ges. Ber.* viii. 1296).

Coal-tar Cumene. The portion of coal-tar naphtha thus designated is a mixture of two trimethyl-benzenes, viz. mesitylene and pseudocumene, which may be separated by the different solubilities of their sulphamides in alcohol (see TRIMETHYL-BENZENES).

CUMENYLAMINE } (so-called); see CYMYL-CARBAMIDE (p. 392).
CUMENYL-UREA }

CUMENYL-ACRYLIC, CUMENYL-CROTONIC, and CUMENYL-ANGELIC ACIDS; see CINNAMIC ACIDS, HOMOLOGUES OF (pp. 501–503).

CUMIC ACID, $C^{10}H^{12}O^3$. Paterhò and Fileti (*Gazz. chim. ital.* v. 383) have demonstrated the existence of two amidocumic acids, $C^{10}H^{11}(NH^2)O^3$. Nitrocumic acid was prepared by dissolving pure cumic acid in four times its weight of well-cooled nitric acid (sp. gr. 1.47), heating for a few minutes, precipitating by water, and crystallising the product first from ether and then from benzene. The purified acid appeared homogeneous and melted at about 157° . It was reduced to the amido-acid by means of iron and acetic acid, the iron removed by sodium carbonate, and the acid precipitated as a lead compound by lead acetate. This was subsequently decomposed by sulphuretted hydrogen, and the amidocumic acid crystallised from boiling water. The first experiment yielded large, transparent, tabular crystals melting at 104.4° , but in all the subsequent operations the product formed acicular scales melting at 129° . The plates melting at 104.4° moreover, after they had been kept for six or seven weeks, also melted at 129° . The acid melting in the first instance at 104.4° (described in vol. ii. p. 170 as *oxycuminamic acid*) was not obtained in any subsequent experiment. The existence of two isomeric amidocumic acids points to the existence of two corresponding nitro-acids; but as the nitrocumic acid appeared perfectly homo-

CUMIC ALDEHYDE—CUMULATIVE RESOLUTION. 593

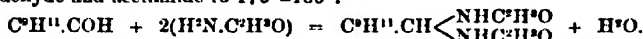
geneous, it is not improbable that it gives rise in the first instance to the amido-acid melting at 104.4° , which is subsequently transformed into the one melting at 129° .

CUMIC ALDEHYDE or **CUMINOL**, $C^{10}H^{12}O = C^8H^{11}.CHO = C^8H < \begin{smallmatrix} C^2H \\ COH \end{smallmatrix}$. This compound boils at 230° , and when heated with hydrocyanic and hydrochloric acids, is converted into phenyl-propyl-glycollic acid, $C^8H < \begin{smallmatrix} C^2H \\ CHOH-CO.H \end{smallmatrix}$.



This acid forms small white needles, melting at 158° . Its *barium salt*, $(C^{11}H^{12}O^2)^2Ba + 4H^2O$, separates from water in small rhombic tables, which lose their water at 120° – 130° . The *silver salt* forms tufts of small anhydrous needles. The *lead salt*, $(C^{11}H^{12}O^2)^2Pb$, forms a white precipitate.

Cuminyl-diacetamide, $C^8H^{11}.CH < \begin{smallmatrix} HNC^2H^3O \\ HNC^2H^3O \end{smallmatrix}$, is obtained by heating a mixture of cumic aldehyde and acetamide to 170° – 180° .



It is sparingly soluble in water, from which it separates in small silky needles melting at 212° , and hot hydrochloric acid splits it up into cuminal and ammonium chloride.

Cuminyl-dibenzamide, $C^8H^{11}.N^2O^2 = C^8H^{11}.CH < \begin{smallmatrix} NH.C^6H^5O \\ NH.C^6H^5O \end{smallmatrix}$ is obtained by heating cumic aldehyde with benzamide. It separates from alcohol in white shining needles, which melt at 224° , and are insoluble in water (A. Raab, *Deut. Chem. Ges. Ber.* viii. 1148).

Hydrocuminamide, $C^8H^{11}.N^2 = (C^8H^{11}.CH)^2.N^2$. This compound, homologous with hydrobenzamide, is formed by heating cuminal to 100° with aqueous ammonia. It is a thick liquid, which, by prolonged heating to 120° – 130° , is converted into an isomeric base, crystallising from alcohol in bulky flocks, from benzene in small nodules, which under the microscope are seen to consist of fine needles. It melts at 205° , is insoluble in water, but dissolves in 38 parts of boiling alcohol, and very readily in benzene and paraffin oils, also in alcohol acidulated with sulphuric acid. It forms salts with sulphuric, nitric, and oxalic acids (Borodin, *Deut. Chem. Ges. Ber.* vi. 1253).

CUMIDINE. Hofmann, in 1872, described under this name a base, the hydriodide of which was obtained by molecular transformation of trimethylphenylammonium iodide (2nd Suppl. 57). Subsequent experiments, however (*Deut. Chem. Ges. Ber.* viii. 61), have shown that this base is really mesidine, $C^6.NH^2.CH^3.H.CH^3.H.CH^3$ (q. v.)

CUMINOL-URETHANE. See CARBAMATES, p. 384.

CUMOL, $C^8H^{10}O = C^8H^9(C^2H^3).OH$. *Cumophenol* (Paternò & Spica, *Gazz. chim. ital.* vi. 535).—This compound is prepared by fusing potassium cumenesulphonate with potash, acidifying the aqueous solution of the fused mass, dehydrating the crude oily product thereby separated, and purifying it by fractional distillation. Cumol crystallises in colourless needles, which melt at 61° . It boils at 228.2° – 229.2° (cor.) under a pressure of 758.18 (cor. to 0°). The *methyl derivative*, $C^8H^9(C^2H^3).OCH^3$, was prepared by heating a solution of equal molecular weights of cumol and potassium hydroxide in methyl alcohol, with a slight excess of methyl iodide. It is a colourless highly refractive liquid, having an odour of aniseed. Its specific gravity at 0° is 0.962, and it boils at 212° – 213° (cor.) under a pressure of 758.04. The *acetyl-derivative*, $C^8H^9(C^2H^3).OC^2H^3O$, was obtained by acting on cumol with excess of acetyl chloride. Its specific gravity at 0° is 1.026, and it boils at 244° – 244.5° (cor.) under a pressure of 756.27.

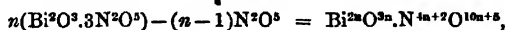
To ascertain the constitution of the cumol prepared in the manner above described, its methyl-derivative was oxidised with a mixture of potassium bichromate and sulphuric acid. A small quantity of an acid was thus obtained, which from its melting point appeared to be anisic acid. If this is confirmed, the cumol must be a para-derivative of benzene.

CUMONITRIL, $C^8H^{11}.N$. This body is formed from thiocuminamide, $NH^2.C^8H^{11}S$, by prolonged boiling with concentrated potash or soda-ley (which abstract SH^2), but is at the same time resolved, by assumption of the elements of water, into cumic acid and ammonia (Wanstrat, *ibid.* vi. 332).

CUMULATIVE RESOLUTION. In the course of his investigations into the nature of the polyalcohols, it was observed by Wurtz (*Leçons de Phil. Chim.* 181) that certain oxides and hydrates are capable of combining with themselves, simultaneously eliminating water; and he gave several instances, especially among polyglyceric and polysilicic compounds, in which the performance of this operation several times in

succession upon the same hydrate was lucidly illustrated. Watts subsequently (in Fownes's *Manual of Chemistry*, 1863, pp. 666, 683) wrote general equations in terms of n for the coincident dehydrating and accumulating processes, whereby the polyglyceric and polyglucosic alcohols are formed. Mills has since (*Phil. Mag.* June, 1877) further developed the theory of this now very frequent phenomenon, to which he applies the term 'cumulative resolution.'

Cumulative resolution is defined as the combination of a substance or mixture of substances with itself n times, a particular portion of it being lost each time, according to some fixed law. Thus, bismuthic nitrate, when decomposed by a gradually increasing quantity of water, yields a series of bodies which are less and less nitrogenous, and more and more bismuthic. Having regard to the denitration alone, we write:

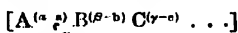


and, by giving various values to n , from 0 to ∞ , we shall obtain the formulæ of all possible compounds between $\text{Bi}^2\text{O}^3 \cdot 3\text{N}^2\text{O}^5$ and $\text{Bi}^2\text{O}^3 \cdot \text{N}^4\text{O}^{10}$. But it is obvious that this latter compound is capable of undergoing precisely the same operation as its predecessor; so that, taking a second time, and in a new equation, a set of values of n from 0 to ∞ , we arrive at the formula $\text{Bi}^2\text{O}^3 \cdot \text{N}^2\text{O}^5$. And upon this we can perform the same operation once more, but evidently only once more; the final result, this third time at infinity, being the expression Bi^2O^3 . According to this mode of representation of the reaction, the passage from one multiple proportion to another in bismuthic nitrate contains an indefinitely great number of terms, of which the 'multiple proportions' are in fact the extreme conditions. In the first stage, bodies are known corresponding to 1 and 1; in the second, for $n=2$; and in the third, for $n=\frac{2}{3}, \frac{1}{3}, \frac{1}{4}, 1$ and ∞ . Thus the whole of these hitherto obscure compounds are included in a clear and systematic theory.

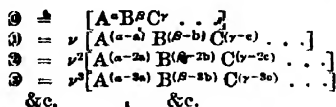
A more general aspect of this common form of cumulative resolution is the following. Let a substance $\text{A}^a\text{B}^b\text{C}^c \dots$ (termed the *diapolyte* by Mills) undergo cumulative resolution, losing $\text{A}^a\text{B}^b\text{C}^c \dots$ (termed the *apolyte*) we may write:



When n becomes exceedingly large with respect to m , the right-hand side of the equation becomes:



Such a product is named a *cumulate*, and is necessarily preceded by some symbol for an infinite value of n . Now there is reason to believe that, when n is very large, the actual chemical condition is one of unstable equilibrium, in anticipation of the next stage of resolution: hence it is uncertain whether the mathematical sign for infinity should be used. In order to avoid this difficulty, the letter ν , when representing a very large number, is written ν , which is accepted in this theory as the symbol for chemical infinity. Cumulates also, on account of their peculiar properties, require a special symbol, for which O (a C reversed) has been proposed as convenient. Returning now to the general equation, it is easy to see that we can obtain from it the following series of cumulates:—



While these differ in composition by a uniform amount, their operator ν proceeds by powers; and the curve representing the relation of ν to their difference is a logarithmic curve. A consideration of the following cases shows that the theory of cumulative resolution must have a wide range of practical application.

1. *Ammonic Carbonates*.—The different ammonic carbonates may be conceivably formed by deammoniating diammonic carbonate or by decarbonating hydroammonic carbonate. [Rose's nine-fourths carbonate is, however, an exception, and does not fall into any system of classification hitherto adduced.] In the latter case the equation is (omitting hydration water)?



The following table contains the known values of the ratio $r = \frac{\text{N}}{\text{C}}$ in the various carbonates, and the corresponding values of n :

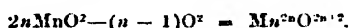
	N : C
0.00	0 : 1
0.16	2 : 7
0.25	2 : 5
1.00	1 : 1
2.00	4 : 3
3.00	3 : 2
4.142857	$\frac{32}{11} : 2$
5.00	5 : 3
7.00	7 : 4
15.00	

Expressing n in terms of r , we have:

$$r = \frac{2n}{n+1},$$

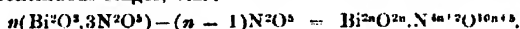
a relation which is graphically expressed by a rectangular hyperbola. This curve is in general the form of transition from one stage to another in cumulative resolution.

Manganic oxides.—The derivatives of manganic dioxide can be represented as follows:—



Known ratios of Mn to O correspond to $n = .5, 1, 1.2, 2, 3$, and ∞ .

Bismuthic nitrates.—The occurrence of these hitherto obscure compounds is, as has been stated, easily intelligible on the principles of cumulative resolution. The action of water on normal bismuthic nitrate is necessarily represented as containing three distinct continuous stages, viz.:

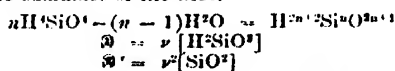


Hence, denitrating thrice, we get:

$$\begin{aligned} 3 &= \nu [\text{Bi}^2\text{O}^3.\text{N}^2\text{O}^5] \\ 3 &= \nu^2 [\text{Bi}^2\text{O}^3.\text{N}^2\text{O}^5] \\ 3 &= \nu^3 [\text{Bi}^2\text{O}^3] \end{aligned}$$

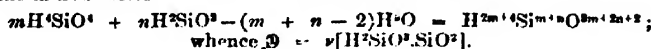
In the first stage, ratios are known for $n = .1$ and 1 ; in the second, for $n = 2$; in the third, for $n = .5, .4, .3, 1$ and ∞ .

Silicates.—A large number of silicates are derivable from two silicic hydrates, of which the second is the cumulate of the first.



After the first cumulate, the second series is $\nu\text{H}^2\text{Si}^n\text{O}^{2n+1}$.

For the mixed series:



The following minerals are members of the series referred to:

Series 1.—Peridot, phenakite, zircon, almandine, grossularin, tetrothylic silicate ($n = 1$).

Analcime? ($n = 1.3$).

Okenite ($n = 2$).

Magnesite, Labradorite ($n = 3$).

Diopside, enstatite, chlorophæite, amphibene, pyrophyllite, tale, emerald, diethylic silicate ($n = \infty$).

Series 2.—Anorthite ($n = 5$).

Fremy's hydrate ($n = 1.5$).

Diethylic disilicate ($n = 3$).

Dover's hydrate ($n = 3$).

Mixed Series.—Orthose ($y = 4, m = 2$).

Analcime ($n = -1, m = 5$).

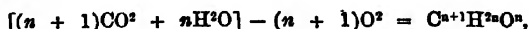
Fuchs's hydrate ($n = \infty, m = \infty$).

Homology.—Taking homologues of any radicle X, we have in general $\text{X.O}^n\text{H}^{2n}$. When n becomes very large, X becomes insignificant; consequently the cumulate in any homologous series is undistinguishable in composition from an olefine. The complexity of any member of a homologous series depends on the value of n and the ratio r of C to H, these being its only variables. In the case of the fatty alcohols:

$$\begin{aligned} &= \frac{2n+2}{q \leq 2} \end{aligned}$$

a hyperbolic relation between r and n . A similar relation holds good in all homologous series except those of the olefines, where $\phi = 0.5$. Omitting this series, it obviously follows that the physical properties of homologous bodies cannot be a linear function of their symbolic value.

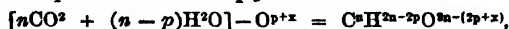
Plant Products.—When a living plant takes up carbonic dioxide and water, it loses oxygen, and forms cellulose, cannose, glucose, glucosides and other products. If we take the equation:



and give successive integral values to n , we obtain the ratio in cellulose, starch, dextrin, or glucosan ($n=5$), hydric kinato ($n=6$), cannose ($n=11$), and glucose ($n=\infty$).

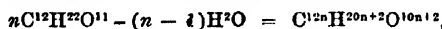
Again, the composition of vegetable acid bodies cannot be represented by a lower formula than CH^2O , nor, according to Debus's law (*Chem. Soc. Jour.* xix. 256), by a higher one than $C^aH^{2a+2}O^{a+1}$, if b stand for 'basicity.' In systematic works, the general type of the formulæ of these bodies is $C^aH^{2a-2p}O^m$.

The cumulative equation is most simply constructed thus:



whence $\mathcal{Q} = \nu(CH^2O^2)$, the ratio $\frac{O^2}{C}$ is the highest permissible in any formula, according to the law referred to, H^2 being a minimum. It appears, then, that (CH^2O) and (CH^2O^2) are the extremes of composition for vegetable acid bodies; their composition, therefore, ranges between that of glucose and hydric carbonate. Glucosides are intermediate between celluloids and acid bodies. The extremes of composition of many other series can be traced in a similar manner.

Caramels.—The results of the organic analysis of these bodies are such as to lead to very complicated formulæ, which cannot be regarded as established on the basis of that method alone. The theory of cumulative resolution easily connects together the whole of these hitherto doubtful substances. Taking



we have $\mathcal{Q} = \nu C^{12}H^{20}O^{10}$, $\mathcal{Q} = C^{12}H^{16}O^9$ (Caramelane), $\mathcal{Q} = \nu C^{12}H^{10}O^8$, $\mathcal{Q} = \nu C^{12}H^6O^7$ (Caramelene), all of which are known. Caramelin seems to be exactly intermediate between \mathcal{Q} and \mathcal{Q} .

Etherification.—The formation of ethers from the fatty alcohols is, in effect, a dehydrating process:—



Hence $\mathcal{Q} = \nu C^2H^4$. In conformity with this result, we find that the action of oil of vitriol on fatty alcohols, when pushed to an extreme, yields ethene and its polymerides, but not methene.

Other Systems of Cumulative Resolution.—The above equations all belong to a simple system in which the exponents of n and $(n-m)$ are both unity. But this is not necessarily always the case that system being, in fact, but a particular instance of a more general one, in which the exponent may have any value whatever. This more general system may be expressed as follows:—

$$n^p(A) - (n-m)^q(A^g),$$

where (A^*) is the diapolyte and (A^g) the apolyte. The cumulate of this expression is $\mathcal{Q} = \nu(A^*) - \nu(A^g)$, representing a body whose composition would differ inappreciably from $(A - A^g)$. This kind of resolution probably occurs in many cases of rapid destructive distillation, p being then much greater than q ; but no instances of it are exactly known. Other systems are readily conceivable, if we affect n and $(n-m)$ with other mathematical functions.

The complementary theory to that of cumulative resolution is that in which the apolyte is regarded as undergoing cumulative composition. This process, however, is one from which apolytes are singularly averse, and its existence at present can only be indicated.

It is obvious that the theory of cumulative resolution—based as it is on the simple device of making n very large in certain chemical equations,—leads to consequences of considerable practical importance, and throws light on many problems which do not admit of direct experimental attack.

E. J. M.

CUPRAMMONIUM SALTS. When alcohol is poured upon a mixture 1 mol. cuprammonium nitrate or sulphate and 7 mol. iodine, explosions take place within the liquid, of various degrees of intensity, but not strong enough to break the

vessel. *Acetyl chloride* and *benzoyl chloride* become strongly heated in contact with cuprammonium sulphate, with production of ammonia and the corresponding acids (Schwarzenbach, *Deut. Chem. Ges. Ber.* viii. 1231).

CUPROSTHIOGLYCOLLIC ACID. See GLYCOLLIC ACIDS.

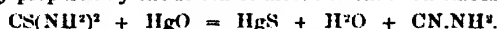
CURARINE. For the method of detecting this base in a mixture of bases, see PLANT-BASES.

CUSCONINE. See CINCCHONA-BASES (p. 406).

CUSPARIN. See ANGUSTURA BARK (p. 87).

CUTOSE. See VEGETABLE TISSUES.

CYANAMIDE, CN.NH_2 , or **CARBODIIMIDE**, $\text{C} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}$. This compound is most conveniently prepared by the action of mercuric oxide on thiocarbamide:



Levigated red mercuric oxide—or better the precipitated oxide—is gradually added to a cold and not concentrated solution of thiocarbamide, and, as soon as all the sulphur is removed, a drop of acetic acid is added to the filtrate, which is then evaporated on a water-bath. The residue dissolves almost completely in ether, and, on evaporating the resulting solution, pure cyanamide is left behind. An excess of mercuric oxide must be carefully avoided. The end of the reaction is easily recognised by dipping a small piece of filter-paper in the liquid, and moistening it with an ammoniacal solution of silver nitrate, which produces a dark coloration, as long as any thiocarbamide remains undecomposed. This reaction is sufficiently delicate to serve for the volumetric estimation of thiocarbamide (Volkard, *J. pr. Chem.* [2], ix. 24).

Cyanamide is very deliquescent, and on evaporating its aqueous or ethereal solution it remains as a liquid, which solidifies when touched with a pointed body. It is but sparingly soluble in carbon sulphide, chloroform, ethidene dichloride, ethyl iodide, amyl bromide, and benzene.

Compounds of Cyanamide with Acids.—The *hydrochloride*, $\text{CN.NH}_2.2\text{HCl}$, is easily obtained by passing dry hydrochloric acid into a solution of cyanamide in pure, dry ether. It is a very bulky, white crystalline powder, which crystallises from water in large plates; it does not combine with the chlorides of platinum or gold. Its aqueous solution gives with silver nitrate a precipitate of silver chloride, but the ammoniacal solution precipitates yellow silver cyanamide. Its constitution may be represented by the formula $\text{HCl.CN.NH}_2\text{Cl}$, analogous to that of the compound of hydrochloric acid and cyanic acid or carbimide, HCl.CN.OH .

The *hydrobromide*, $\text{CN.NH}_2.2\text{HBr}$, is prepared like the hydrochloride, and is a very similar body. The *nitrate*, obtained by passing a mixture of air and nitric acid vapour through an ethereal solution of cyanamide, and evaporating the solution in dry air, is crystalline, but very unstable (Drechsel, *J. pr. Chem.* [2], xi. 284).

Metallic Derivatives of Cyanamide.—The *sodium compound*, CN.NHNa , is formed by adding sodium to a solution of cyanamide in ether, but it is more conveniently prepared by adding to a cold solution of 1 pt. of sodium in 15 of absolute alcohol, an alcoholic solution of 2 of cyanamide in small portions. The bulky precipitate soon changes into a crystalline powder, which may be washed with ether. It is a very fine, light powder, dissolving in water with evolution of heat.

When heated it melts, and then decomposes:



Heated with a small quantity of water in sealed tubes, it yields urea, sodium carbonate, and a small quantity of carbamate.

Its aqueous solution gives precipitates with metallic salts, the reaction with silver nitrate being:



Potassium forms a similar compound.

Silver cyanamide, CN.Ag^+ , obtained by precipitating an aqueous solution of cyanamide with ammoniacal silver nitrate (2nd Suppl. 404), is soluble in nitric acid, nearly insoluble in cold aqueous ammonia, but soluble in the hot liquid, from which it crystallises on cooling in microscopic needles, some of the cyanamide being at the same time converted into dicyanodiamide.

Barium cyanamide is obtained as an amorphous precipitate on mixing solutions of baryta and cyanamide in methyl alcohol.

Copper cyanamide is obtained as a blackish-brown, amorphous precipitate, when solutions of copper acetate and cyanamide are mixed. It is readily soluble in acids and in ammonia, and on exposing the latter solution to the air, the compound separates in indistinctly crystalline globular masses. An ammoniacal solution of cuprous chloride gives with cyanamide a white precipitate which blackens in the air.

Lead cyanamide, CN.NPb .—Cyanamide precipitates neither normal nor basic lead acetate, but on adding a few drops of ammonia, a yellowish amorphous precipitate is formed, which soon becomes crystalline and lemon-yellow, forming scales resembling lead iodide.

A solution of *thallium oxide* gives no precipitate with cyanamide, and a solution of *mercuric chloride* only a small quantity of a white precipitate (Drechsel, *loc. cit.*)

Mercuric Cyanamide, CN^2Hg , is obtained as a white precipitate by acting on cyanamide with mercuric chloride and a little potash, or on a solution of cyanamide with freshly precipitated mercuric oxide (R. Engel, *Bull. Soc. Chim.* [2], xxiv. 909).

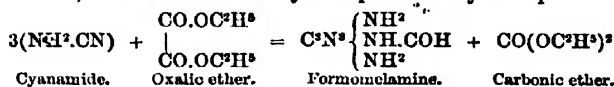
Reactions of Cyanamide.—1. Cyanamide decomposed by the electric current yields hydrocyanic acid, together with other products (E. Mulder, *Deut. Chem. Ges. Ber.* vii. 1634).

2. *Nascent hydrogen* acts slowly on cyanamide, producing ammonia and methylamine, $\text{NH}^2\text{CN} + 3\text{H}^2 = \text{NH}^3 + \text{CH}^3\text{N}$ (Drechsel, *J. pr. Chem.* [2], xi. 284).

3. *Acetyl chloride* converts cyanamide into acetyl-cyanamide, $\text{CN.NH}(\text{C}^2\text{H}^3\text{O})$, which however has not been obtained pure (Drechsel, *J. pr. Chem.* [2], viii. 337).

4. *Benzoyl chloride* and cyanamide do not act upon each other either in presence of ether or when heated together; but benzoyl chloride and dry *sodium-cyanamide*, heated together, give benzoyl-ammeline, benzonitril, carbon dioxide and sodium chloride. Benzoyl-ammeline, $\text{C}^{10}\text{H}^8\text{N}^2\text{O}^2 = \text{C}^3\text{N}^2(\text{OC}^7\text{H}^5\text{O})(\text{NH}^2)^2$, is a yellow mass easily soluble in alcohol, benzene, soda-ley, and acetic acid, sparingly soluble in ether, insoluble in water. Over sulphuric acid it shrinks together to a brown resinous body. Heated in a stream of hydrogen it is resolved into cyanamide, benzonitril, and carbon dioxide. Benzoyl chloride and sodium-cyanamide, acting on one another in presence of ether, form sodium chloride and benzoyl-cyanamide, $\text{CN.NH}(\text{C}^7\text{H}^5\text{O})$, which however quickly decomposes, and partly separates into carbon dioxide, benzonitril, and cyanamide; but by prolonged digestion of its ethereal solution, it is partly converted into tribenzoyl-melamine (see MELAMINE). Benzoyl-cyanamide mixed with *sodium ethylate* in ethereal solution gives sodium-benzoyl cyanamide, $\text{CN.NNa}(\text{C}^7\text{H}^5\text{O})$, which is resolved by heat into sodium cyanate and benzonitril (Gerlich, *J. pr. Chem.* [2], xiii. 270).

5. With *Ethyl oxalate*.—Cyanamide dissolves with oxalic ether, sparingly at ordinary temperatures, easily and without decomposition at the heat of the water-bath (oven in presence of a small quantity of water). But when the two bodies (anhydrous) are heated together to 110° in an open tube, or in a retort fitted with a condenser, reaction gradually takes place, becoming violent if the temperature is raised to 130° . The best product is obtained when the reaction goes on slowly, and an excess of oxalic ether is used (about 4 grams of the ether and 4 grams of cyanamide). The product having been washed with alcohol (undecomposed cyanamide passing into the filtrate), there remains a faint yellow body which may be heated without decomposition to 150° (in contact with oxalic ether, even to 185°), and dissolves in potassium carbonate, from which it is thrown down by nitric acid as a bulky colourless precipitate, soluble in excess of the acid. This body is decomposed by heating with dilute sulphuric acid, hydrochloric acid, acetic acid, and even with water, in which it is insoluble. At a red heat it does not melt, but is converted into a brown product, which burns away with difficulty. The yellow body has the composition of monofomomelamine, and its formation may be represented by the equation:



the reaction between the oxalic ether and the cyanamide being supposed to be attended with polymerisation of the latter (E. Mulder, *Deut. Chem. Ges. Ber.* vii. 1631).

6. Cyanamide boiled with a concentrated solution of *alloxantin*, yields iso-uric acid, $\text{O}^5\text{H}^4\text{N}^4\text{O}^3$, which is deposited in the form of a heavy powder (Mulder, *ibid.* vi. 1233).

7. *Action of Acids*.—Cyanamide brought in contact with concentrated sulphuric acid gives rise to an explosive action. With sulphuric acid, diluted with an equal volume of water, so much heat is developed that the mixture boils. When an excess

of cyanamide has been employed, the liquid, on cooling, deposits a white amorphous precipitate of ammeline, acid ammonium sulphate being formed at the same time:—



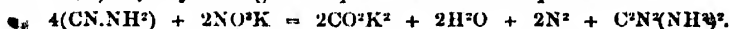
But only a relatively small quantity of cyanamide is decomposed in this way, and when an excess of sulphuric acid is used, this decomposition does not occur. In either case the greater part of the cyanamide is converted into urea, whilst variable quantities of dicyanodiamidine are also produced.

The same products are obtained with 6 per cent. sulphuric acid, and with moderately concentrated phosphoric acid. Hydrochloric acid produces dicyanodiamidine, and probably also urea, but the presence of even a small quantity of dicyanodiamidine greatly interferes with the detection of urea.

When *hydrogen sulphide* is passed into a solution of cyanamide in anhydrous ether, thiocarbamide, $\text{CN}(\text{NH})_2$, separates in shining crystals. The reconversion of this latter compound into cyanamide may be effected by agitating its alcoholic solution with recently precipitated and well-washed mercuric oxide, to which a few drops of hydrochloric acid have been added to neutralise the last traces of alkali. The desulphuration is completed in a short time, and the filtrate contains nothing but cyanamide (Baumann, *Deut. Chem. Ges. Ber.* vi. 1373).

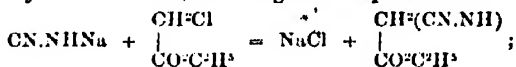
8. *Polymerisation*.— α . Cyanamide heated to 150° in ethereal solution, or to a higher temperature in the dry state, is converted into dicyano-diamide, $\text{C}^{\text{N}}\text{N}^{\text{O}}(\text{NH})_2$ (ii. 189).

Cyanamide is also converted into dicyanodiamide, β . By heating it with water or with dilute alkalis; concentrated alkalis decompose it (Baumann, *Deut. Chem. Ges. Ber.* vi. 1371). γ . By heating it in aqueous solution with potassium nitrite:

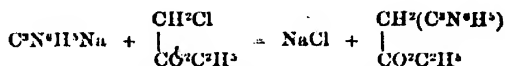


8. Cyanamide heated with *acetamide* and alcohol does not yield acetyl-guanidine, as might be expected, according to the reaction, $\text{CN.NH} + \text{C}^{\text{H}}\text{O}^{\text{O}}\text{N}^{\text{H}} = \text{N}^{\text{O}}(\text{C}^{\text{H}}\text{H}^{\text{O}}\text{O}^{\text{H}}\text{O})$, but only dicyanodiamide, the acetamide and alcohol acting on each other so as to form acetic ether and ammonia

ϵ . Sodium-cyanamide heated with *ethyl monochloracetate* and alcohol, might be expected to yield cyanamidacetic acid, according to the equation:



but instead of this, the group CN.NHNa is converted, by polymerisation of the organic molecule, into $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{N}^{\text{H}}\text{Na}$, which reacts in like manner with the chloroacetic ether, forming melidacetic acid, $(\text{C}^{\text{H}}\text{H}^{\text{O}}\text{N}^{\text{H}})\text{CH}^{\text{O}}\text{COOH}$, i.e. acetic acid in which 1 atom of hydrogen is replaced by melamide, $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{N}^{\text{H}}$ (or melamine, $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{N}^{\text{H}}$, minus an atom of hydrogen):



Melidacetic acid is a white chalky powder, dissolving but sparingly in cold water, slowly but freely in boiling water, insoluble in alcohol and ether, somewhat poisonous. From the boiling aqueous solution it crystallises by slow cooling in white needles, by quick cooling in silky plates. Like other amido-acids, it unites with acids as well as with bases.

The *hydrochloride*, $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{N}^{\text{H}}\text{HCl}$, is slightly soluble in cold, more freely in boiling water, and crystallises in brilliant white needles which are insoluble in concentrated solutions.

In solution, the compound $\text{C}^{\text{H}}\text{H}^{\text{O}}\text{N}^{\text{H}}\text{NO}^{\text{O}}\text{Ag} + \text{H}^{\text{O}}$ separates in white needles, which dissolve readily in hot, but are almost insoluble in cold water. The *sulphate*, $(\text{C}^{\text{H}}\text{H}^{\text{O}}\text{N}^{\text{H}})_2\text{SO}^{\text{O}}\text{H}^{\text{O}}$, crystallises from hot water in large thick prisms. The *phosphate* separates from a hot solution in needles.

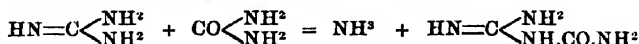
The melidacetates of the alkali-metals are easily soluble in water, and are precipitated by alcohol as crystalline powders (Drechsel, *J. pr. Chem.* [2], xi. 284).

Dicyanodiamide, $\text{C}^{\text{N}}\text{H}^{\text{O}}$, or $\text{HN}=\text{C} \begin{array}{c} \text{NH} \\ \text{NH} \end{array} \text{C}=\text{NH}$. This polymeride of cyanamide (formerly called *Param*) is formed, as above stated, by heating cyanamide either alone, or in ethereal solution, or with water, or with dilute alkalis. When heated it melts and gives off ammonia, and on increasing the heat, more ammonia

escapes, a white crystalline sublimate forms, and a yellow residue is left, consisting of melamine, $C^3H^3N^3$ (Drechsel, *J. pr. Chem.* [2], xiii. 330).

Argento-dicyanodiamide, $C^2N^4H^2Ag$, according to Haag, $C^2N^4H^2Ag^2$, according to Engel, is obtained by treating dicyanodiamide with silver nitrate, and adding ammonia (not in excess) or potash, to the products, as a white precipitate soluble in ammonia. The mercuric compound, $C^2N^4H^2Hg$, formed on adding mercuric chloride and a little potash to dicyanodiamide, is a white body sparingly soluble in acetic acid, more freely in hydrochloric acid (Engel, *Bull. Soc. Chim.* [2], xxiv. 272).

Dicyanodiamidine, $C^2N^4H^2O = HN=C<\begin{smallmatrix} NH^2 \\ NH.CO.NH^2 \end{smallmatrix}$ (Haag, *Liebig's Annalen*, cxxii. 22; Baumann, *Deut. Chem. Ges. Ber.* vii. 446, 1766). This base is formed by the action of dilute acids on dicyanodiamide, $C^2N^4H^4 + H^2O = C^2N^4H^2O$; also by fusing the carbonate or other salt of guanidine with urea:

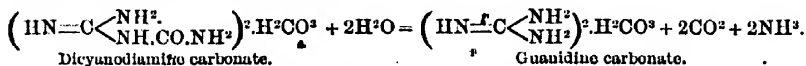


This reaction establishes the constitutional formula of dicyanodiamidine (first suggested by Strecker), and moreover affords the readiest mode of preparing it. 2-2½ pts. of dry urea are heated to 150°-160°, with 1 pt. of dry guanidine carbonate (the other guanidine salts do not give good results): the resulting dicyanodiamidine is separated from other products of decomposition of urea and guanidine, by dissolving the melt in water, adding a little caustic soda, and then cupric sulphate, as long as the rose-coloured precipitate thereby formed continues to increase; and the precipitate is collected on a filter, washed and purified by one crystallisation, whereby it is obtained in microscopic crystals. This compound decomposed by hydrogen sulphide yields dicyanodiamidine (Baumann).

The substituted guanidines when fused with urea appear to yield substitution-derivatives of dicyanodiamidine.

The free base may be obtained by decomposing the hydrochloride with silver oxide; it is strongly alkaline, and absorbs carbonic anhydride from the air. The solution, evaporated over sulphuric acid, gives crystals resembling those of urea; they are easily soluble in alcohol, and the addition of ether to the solution produces a slight crystalline precipitate.

The *neutral carbonate*, $(C^2N^4H^2Q^2) \cdot H^2CO^3$, is formed by decomposing a concentrated solution of the sulphate with barium carbonate suspended in water. On evaporating the solution over sulphuric acid till it becomes a syrup, needles are deposited, which, however, cannot be separated from the mother-liquor in a state fit for analysis. If the solution of the carbonate is evaporated at 100°, ammonia and carbonic anhydride are given off; and the addition of alcohol throws down crystals of guanidine carbonate, $CN^2H^3 \cdot H^2CO^3$, easily soluble in water, but only slightly soluble in alcohol; they are identical with those which Haag described as hydrated dicyanodiamidine. This decomposition, which takes place slowly at ordinary temperatures, is represented by the equation:



The *acid carbonate*, or *dicarbonate*, $C^2NH^2Q \cdot H^2CO^3$, is formed when carbonic anhydride is passed into a moderately dilute solution of the neutral carbonate, and settles down gradually in the form of a crystalline precipitate, which may be purified by washing it on a filter with alcohol, and drying it over sulphuric acid. Under the microscope, it appears to be made up of slender concentrically grouped needles. It is sparingly soluble in water (in 150 pts. at 18°), permanent in dry air at ordinary temperatures, but is resolved by prolonged heating at 100°, into neutral dicyanodiamidine carbonate and guanidine carbonate, together with carbon dioxide and ammonia:



When boiled with water it is decomposed in the same manner as the neutral carbonate.

The compounds of dicyanodiamidine with the stronger acids are very stable, not undergoing the slightest decomposition when their solutions are boiled, or when they are treated with mercuric oxide. When mixed in acid solution with *potassium chlorate* and evaporated over the water-bath, they are decomposed, with formation of guanidine, according to the equation:



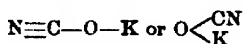
When a solution of dicyanodiamidine sulphate or carbonate is boiled with excess

of barium hydrate, barium carbonate is precipitated, ammonia evolved, and the clear solution on evaporation yields urea—

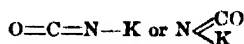


Dicyanodiamidine sulphate and hydrochloride, when heated, completely decompose into ammonium salts, ammonia, and a white amorphous body, slightly soluble in cold, easily in hot water, and possessing feeble basic properties. It is soluble in acids and alkalis, forming crystalline compounds with the first, which, however, are easily decomposed.

CYANATES. Metallic cyanates admit of two modifications analogous to those of the cyanic ethers (1st Suppl. 519), e.g.:



Normal Cyanate.



Isocyanate.

Of the normal cyanates, only one is at present known, viz., the potassium salt, which Bannow obtained by the action of caustic potash on cyanogen chloride:



also by the action of potash on paracyanogen, and by heating the ordinary cyanate with cyanogen iodide (2nd Suppl. 405). It crystallises from alcoholic solution in long thin needles, whereas ordinary potassium cyanate crystallises in scales resembling the chlorate. Its mode of formation shows that it contains the group CN, and has its metallic element united to the carbon through the medium of oxygen, a constitution analogous to that of the normal cyanic ethers. Hence it follows that the ordinary potassium cyanate and the other metallic cyanates are isocyanates or derivatives of carbimide, containing the group CO, and having their metallic element united to the carbon through the medium of nitrogen.

Hydrogen cyanate or cyanic acid is known in one modification only, and as this is produced by reactions analogous to those which give rise to the ordinary metallic cyanates (ii. 190), it is most probably isocyanic acid, or carbimide, $\text{CO}=\text{N}-\text{H}$. On the constitution of cyanic acid, see further Fleischer (*Deut. Chem. Ges. Ber.* ix. 436); Michler (*ibid.* 715); Claus (*ibid.* 721); also *Chem. Soc. J.* 1878, ii. 73, 288; *Jahresb. f. Chem.* 1876, 308.

Preparation of Potassium (iso)Cyanate.—The following modification of Liebig's well known process for the preparation of ordinary potassium cyanate has been proposed by C. A. Bell (*Chem. News*, xxxii. 99). Four parts of perfectly dried and finely pounded potassium ferrocyanide are intimately mixed with three parts of dry and pulverised potassium dichromate. A small quantity of this mixture is placed in a porcelain or iron dish, the temperature of which is then raised until a tinder-like combustion takes place, and the mixture blackens, which happens considerably below a red heat. The rest of the mixture is then thrown in by small quantities at a time, each successive portion being allowed to blacken completely before it is covered by the next. This is necessary, for if air be excluded during the combustion, a considerable quantity of potassium cyanide will be found unoxidised.

When all the mixture has been added, the dish is allowed to cool. The result of the reaction is a porous friable mass, from which the cyanate may be extracted with boiling alcohol. To diminish as much as possible the loss from conversion of the cyanate into carbonate during boiling, and also to economise alcohol, it is advisable to add to the latter at each boiling only about as much of the mixture as can be thoroughly exhausted by it. The crystallisation of the cyanate may be hastened by immersing the vessel containing the alcoholic solution in cold water. In a favourable experiment the resulting cyanate, equal to about 42 per cent. of the dried ferrocyanide, contained less than 1 per cent. of impurity.

To obtain the insoluble cyanates, lead, silver, &c., it is only necessary to exhaust the black mass with very cold water, remove the chromate and unaltered ferrocyanide with barium nitrate, and finally to precipitate with a nitrate of the metal.

From the above aqueous solution urea may be prepared by the addition of 4½ pts. of ammonium sulphate, evaporation to dryness, extraction with boiling alcohol, &c., or better with amylic alcohol.

Allyl Isocyanate or **Allyl-carbimide**, $\text{CO}=\text{N}-\text{C}^2\text{H}_5$, is formed, together with sodium monosulphide, by the action of sodium-amalgam on allyl thiocyanate Billster, *Deut. Chem. Ges. Ber.* viii. 464).

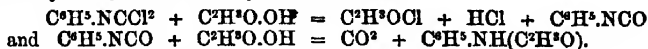
Methyl Isocyanate acts on methyl-succinimide, with formation of ill-defined products. **Ethyl isocyanate** does not unite either with methyl- or with ethyl-succinimide (Menschutkin, *Petersb. Acad. Bull.* xxi. 25).

Pseudopropyl Cyanate, $\text{CN.O.CH(CH}^3\text{)}^2$, obtained by treating the iodide with silver cyanate, boils at 74° (Silva, *Bull. Soc. Chim.* [2], xvii. 97).

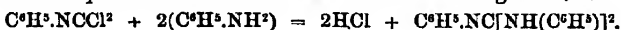
Phenylic Isocyanochloride, $\text{C}^6\text{H}^5\text{—N=CCl}^2$, is formed by saturating a solution of phenyl isocyanate in chloroform with chlorine:



The product is a yellowish heavy liquid boiling at $211^\circ\text{--}212^\circ$, and emitting a very pungent vapour which violently attacks the mucous membranes. It acts readily on *glacial acetic acid*, with evolution of HCl and CO^2 , and formation of acetic chloride, phenyl isocyanate, and ultimately acetanilide:



Phenylic isocyanochloride is violently attacked by dry *silver oxide*, with formation of phenyl isocyanate, and partial carbonisation. By *hydrogen sulphide* the chloride is completely reconverted into phenyl isocyanate. With *aniline* the chloride yields an isomide of triphenyl-guanidine, the hydrochloride of which crystallises from aqueous alcohol in small white laminae melting at 207° :



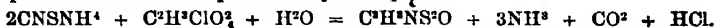
Phenylic isocyanochloride, heated to 100° in sealed tubes with water, yields diphenyl-carbamide, $\text{CON}^2\text{H}^2(\text{C}^6\text{H}^5)^2$, and aniline hydrochloride; with *methyl* and *ethyl alcohol* it yields the phenylic urethanes, $\text{CO} \begin{smallmatrix} \text{OCH}^3 \\ \text{NH.C}^2\text{H}^5 \end{smallmatrix}$ and $\text{CO} \begin{smallmatrix} \text{OC}^2\text{H}^5 \\ \text{NH.C}^2\text{H}^5 \end{smallmatrix}$ with separation of HCl and CH^3Cl , or $\text{C}^2\text{H}^5\text{Cl}$.

In the preparation of phenylic isocyanochloride, more highly chlorinated products are also formed. Thus on treating a product not purified by fractional distillation with aqueous ammonia, the compound $\text{C}^6\text{H}^5\text{Cl.NC(OH)(NH}^2\text{)}$ was formed, indicating the presence of a chlorinated phenylic isocyanochloride in the crude products. It crystallised in white plates, and yielded chloraniline when distilled with potash (Sell a. Zierold, *Deut. Chem. Ges. Ber.* vii. 1228).

THIOCYANATES, CN—S—R .

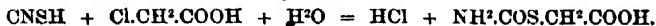
Colour-reactions of Thiocyanic acid.—Many substances, chiefly organic, as cork, wood, cotton, silk, skin, horn, &c., produce, with free thiocyanic acid, a red coloration similar to that produced with ferric salts; hence in testing for iron with potassium thiocyanate, care must be taken that the solutions employed are neutral (Miquel, *Bull. Soc. Chim.* [2], xxvi. 442).

Reactions of Thiocyanic acid and its salts with Monochloroacetic acid.—Ammonium thiocyanate and chloroacetic acid act strongly on one another when gently heated together, forming rhodanic acid, $\text{C}^2\text{H}^3\text{NS}^2\text{O}$ (q. v.), a crystalline substance, very slightly soluble in cold, more freely in hot water, easily soluble in alcohol, ether, ammonia, and in the fixed alkalis and their carbonates. Its formation appears to take place in the manner represented by the equation:



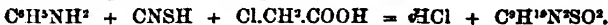
The same compound is formed by the action of chloroacetic acid on other thiocyanates (Nencki, *J. pr. Chem.* [2], xvi. 1).

When, on the other hand, chloroacetic acid acts on free thiocyanic acid, the product consists of carbaminthiacetic acid, $\text{C}^2\text{H}^3\text{NSO}^2$:



This acid is soluble in alcohol and ether, melts at 143° , and when heated yields thioglycollic acid. None of its metallic salts have been obtained. In cold aqueous solution it is easily resolved into cyanic and thioglycollic acids (Nencki).

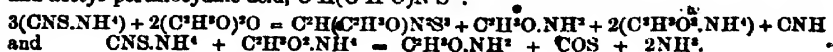
When chloroacetic acid is heated with thiocyanic acid and aniline in alcoholic solution, the following reaction takes place:



The compound $\text{C}^6\text{H}^5\text{N}^2\text{SO}^2$, thus obtained forms crystals which under the microscope exhibit the form of long flattened prisms, apparently orthorhombic. It is insoluble in cold water, moderately soluble in hot water, sparingly in ether. *Toluidine* treated with thiocyanic and chloroacetic acids yields the homologous compound $\text{C}^7\text{H}^7\text{N}^2\text{SO}^2$, which exhibits similar properties (J. H. Jäger, *J. pr. Chem.* [2], xvi. 17).

Reaction of Ammonium Thiocyanate with Acetic acid and Anhydride.—When ammonium thiocyanate (3 mol.) and acetic anhydride (2 mol.) are heated together on

a water-bath to about 80°, gases are given off consisting of hydrogen cyanide and carbon oxy sulphide, with smaller quantities of carbon dioxide and hydrogen sulphide, and the liquid solidifies to a crystalline mass consisting of ammonium acetate, acetamide, and acetyl-perthiocyanic acid, $C^2H(C^2H^2O)N^2S^2$:



When, on the other hand, ammonium thiocyanate and acetic anhydride in equal numbers of molecules are heated together to nearly the boiling point of the latter, no acetyl-perthiocyanic acid is formed, but the liquid becomes turbid from separation of sulphur, and on continued heating, small quantities of unaltered acetic anhydride and carbon disulphide distil over; the temperature then rises quickly to 218°–220°, ammonia is given off, and the crystalline distillate consists almost wholly of acetamide.

Ammonium thiocyanate, gently heated with *acetic acid*, likewise yields acetyl-perthiocyanic acid :



Ammonium thiocyanate and fused *benzoic acid* heated together yield nothing but hydrogen sulphide and benzonitril (Nencki & Leppert, *Deut. Chem. Ges. Ber.* v. 902).

Double salts of Ammonium Thiocyanate (A. Fleischer, *Liebig's Annalen*, clxxix. 225).

Ammonio-mercuric Thiocyanate, $Hg(CNS)^2.2NH^4CNS$.—When yellow mercuric oxide is added to a hot aqueous solution of ammonium thiocyanate, and the liquid quickly filtered while hot, it deposits tabular crystals of the compound $4Hg(CNS)^2.6NH^4.2H^2O$, which, when boiled with water, is converted into mercuric orthothiocyanate, $Hg^2C^2N^2S^2O^2 = Hg(CNS)^2.3HgO$.* This last compound decomposes with explosive violence when heated. On dissolving it in an aqueous solution of ammonium thiocyanate, or on heating mercuric thiocyanate with the same solution, ammonio-mercuric thiocyanate is obtained in monoclinic prisms.

Ammonio-argentic Thiocyanate, $AgCNS.(NH^4)CNS$, prepared in like manner with silver oxide, crystallises in white shining needles.

Ammonio-platinic Thiocyanate is obtained in two modifications by spontaneous evaporation of a mixture of the solutions of ammonium platinochloride and ammonium thiocyanate. One of these modifications forms small scarlet prisms or hexagonal laminae having a bitter taste; the other forms brown-red crystals, tasteless and insoluble in water. **Platinum-potassium Thiocyanate** is prepared in like manner. In this salt the potassium may be replaced by aniline, yielding a substance insoluble in water, but easily soluble in alcohol and ether (Skey, *Chem. News*, xxx. 25).

Zinc-ammonium Thiocyanate, $\begin{matrix} H^2N-S-CN \\ \diagup Zn \\ H^2N-S-CN \end{matrix}$, is prepared from zinc-oxide and ammonium thiocyanate.

Potassium Thiocyanate, $CNKS$. W. Skey (*Chem. News*, xxvii. 179) prepares this salt by boiling flowers of sulphur for a few minutes with water to remove adhering air, and adds to the liquid, after cooling, the calculated quantity of potassium cyanide. The reaction is complete in a few days. Access of air must be prevented and the potassium cyanide must be free from caustic potash, as otherwise potassium sulphide will be produced.

Potassium thiocyanate, treated in alcoholic solution with *phosphorus trichloride*, yields the compound $C^2H^2N^2S^2O$, which crystallises in white needles. With *benzoyl chloride* the compound $C^2H^2S^2O$ is formed, which crystallises in long yellow needles (Lössner, *J. pr. Chem.* [2], vii. 474).

Potassio-platinic Thiocyanate, $(CNS)^2PtK^2 + 2H^2O$, is formed on mixing a warm and moderately concentrated solution (about 10 per cent.) of potassium thiocyanate with a small quantity of solution of platinum tetrachloride. The liquid on cooling deposits the hydrated salt in small very brilliant crystals belonging to the monoclinic system: $a : b : c = 1.566 : 1 : 1.534$. Angle $bc = 80^\circ 46'$ (Wyrouboff, *Ann. Ch. Phys.* [5], xi. 417). Buckton (v. 511) by pouring a solution of platinum tetrachloride into a strong solution of potassium thiocyanate previously heated to 70° or 80°, or

* This salt is regarded by J. Philipp (*Liebig's Annalen*, clxxx. 241) as an amido-compound, inasmuch as it contains a quantity of nitrogen larger than that which is required by the sulphur present for the formation of thiocyanic acid. Philipp represents its constitution by the formula $Hg < \begin{matrix} ^{NH} \\ ^{SH} \end{matrix} HgO$.

by adding 4 pts. potassium platino-chloride to a solution of 5 pts. potassium thiocyanate (weighed in the fused state) in a moderate quantity of water, obtained the same salt in anhydrous six-sided prisms or laminae of a deep red colour.

Ferromercuric Thiocyanate is obtained in long, black, prismatic crystals, on mixing the ethereal solutions of ferric thiocyanate and a mercury salt. It is nearly insoluble in water—which, however, turns it white—also in acetic acid, but soluble in alcohol and in ether. *Ferro-auric Thiocyanate*, prepared in like manner, is finely granular, nearly black, slightly soluble in water, more freely in alcohol and in ether.—*Cobalto-mercuric Thiocyanate* is obtained in two modifications, one forming small, anhydrous, deep blue, almost black crystals, the other light blue prisms of larger size. Both are nearly insoluble in water, and are decomposed by ferric chloride, with formation of ferric thiocyanate.—*Molybdo-mercuric Thiocyanate* is precipitated from aqueous solutions in red flocks (Skey, *loc. cit.*)

Thiocyanates with Mercuric Cyanide. $\text{Hg}(\text{CN})^2 \cdot \text{KCNS}$ forms white shining needles, permanent in the air, easily soluble in hot water.— $\text{Hg}(\text{CN})^2 \cdot \text{NH}_4\text{CNS}$ resembles the potassium salt.— $\text{Hg}(\text{CN})^2 \cdot \text{NaCNS} + 2\text{H}_2\text{O}$ forms colourless needles, which lose their crystallisation-water on exposure to the air.— $2\text{Hg}(\text{CN})^2 \cdot \text{Ba}(\text{CNS})^2 + 4\text{H}_2\text{O}$: four- or six-sided nacreous plates, soluble in hot water and permanent in the air. $2\text{Hg}(\text{CN})^2 \cdot \text{Sr}(\text{CNS})^2 + 4\text{H}_2\text{O}$: thin, nacreous plates, which give off $2\text{H}_2\text{O}$ on exposure to the air.— $2\text{Hg}(\text{CN})^2 \cdot \text{Ca}(\text{CNS})^2 + 8\text{H}_2\text{O}$: large tabular crystals which give off $5\text{H}_2\text{O}$ over sulphuric acid, and the remaining $3\text{H}_2\text{O}$ at 130° – 140° .— $2\text{Hg}(\text{CN})^2 \cdot \text{Mg}(\text{CNS})^2 + 4\text{H}_2\text{O}$: needles permanent in the air.— $2\text{Hg}(\text{CN})^2 \cdot \text{Zn}(\text{CNS})^2 + 4\text{H}_2\text{O}$: small, slightly soluble prisms, permanent in the air.— $2\text{Hg}(\text{CN})^2 \cdot \text{Zn}(\text{CNS})^2 \cdot 3\text{NH}_3$: shining needles, which do not give off their ammonia either on exposure at ordinary temperatures or when heated to 100° , but are decomposed by water, with formation of a white precipitate. $2\text{Hg}(\text{CN})^2 \cdot \text{Cd}(\text{CNS})^2 + 4\text{H}_2\text{O}$: small crystals, permanent in the air, soluble in water. $2\text{Hg}(\text{CN})^2 \cdot \text{Mn}(\text{CNS})^2 + 4\text{H}_2\text{O}$: small, slightly soluble needles.— $2\text{Hg}(\text{CN})^2 \cdot \text{Fe}(\text{CNS})^2 + 4\text{H}_2\text{O}$: small, greenish, six-sided plates.— $2\text{Hg}(\text{CN})^2 \cdot \text{Co}(\text{CNS})^2 + 4\text{H}_2\text{O}$: yellow pointed needles, which are moderately soluble in water, and give off their crystallisation-water at 110° , turning blue at the same time.— $2\text{Hg}(\text{CN})^2 \cdot \text{Ni}(\text{CNS})^2 + n\text{H}_2\text{O}$: amorphous, greenish precipitate.— $2\text{Hg}(\text{CN})^2 \cdot \text{Cu} \begin{smallmatrix} 2\text{NH}_3\text{CNS} \\ 2\text{NH}_4\text{CNS} \end{smallmatrix}$: shining dark blue plates, decomposed by water,

Ethylamine Thiocyanate, $\text{CN} \cdot \text{S} \cdot \text{NH}_2(\text{C}_2\text{H}_5)$, is obtained by heating ethylamine hydrochloride with potassium thiocyanate in aqueous solution, evaporating to dryness, heating the residue for some time to 100° , and digesting it in water. The resulting solution deposits crystallised ethylamine thiocyanate, which is very deliquescent, and gives with ferric salts the red coloration characteristic of the thiocyanates. It is not converted into the isomeric compound, ethyl-thiocarbamide, $\text{NH}_2\text{CS} \cdot \text{NH}(\text{C}_2\text{H}_5)$, either during its preparation or when heated to 150° in sealed tubes. The same is the case with thiocyanate of amylamine, whence it appears that the molecular transformation of the thiocyanates of monamines into the corresponding thiocarbamides, which is easily accomplished in the aromatic series, *e.g.* of aniline thiocyanate into phenyl-thiocarbamide (p. 396), does not take place in the fatty series. Moreover this change does not ensue when thiocyanic acid is heated with free aniline even to 190° , neither is it determined by the presence of chloride of potassium or ammonium; it appears therefore to result from the reaction between thiocyanate of potassium or ammonium and the hydrochloride of the organic base (Ph. de Clermont, *Bull. Soc. Chim.* [2], xxvii. 198).

Melamine Thiocyanate, $\text{C}_3\text{N}_6\text{H}_6\text{CNSH}$, is formed by quickly heating ammonium thiocyanate to 250° , and maintaining this temperature till the whole mass becomes solid. The interspaces of the crude melam thus produced are filled with a fine white sublimate of melamine thiocyanate, consisting of small prisms, which may be dissolved out by warm water. The solution on cooling deposits prismatic crystals, generally of a faint yellowish colour; they are soluble in alcohol, and when carefully heated sublime without change (A. Claus, *Deut. Chem. Ges. Ber.* ix. 1915).

Thiocyanates of Acid Radicles.

These compounds are prepared by the action of acid chlorides on thiocyanate of lead; the mercury, potassium, and sodium salts cannot be used for the purpose (Miquel, *Ann. Chim. Phys.* [5], xi. 289).

a. Inorganic. *Silicon Thiocyanate*, $\text{Si}(\text{CNS})^4$, prepared by the action of silicon tetrachloride on lead thiocyanate, melts at 142° , and boils at 300° . Its vapour burns

in the air with a lilac flame, and is decomposed by passing through a red-hot tube. It is insoluble in anhydrous ether, carbon disulphide, and petroleum, but dissolves in a solution of thiocyanic acid in benzene, and separates therefrom on evaporation in rectangular prisms. It is decomposed by moisture, forming thiocyanic acid and silica; with alcohol, it yields ethyl silicate and thiocyanic acid. The crystals impart a red stain to paper, cotton, the skin, and other organic bodies.

Arsenious Thiocyanate, $\text{As}(\text{CNS})^3$, resembles the preceding compound in its properties and mode of preparation, but is much more difficult to isolate.

Phosphorus Thiocyanate, $\text{P}(\text{CNS})^3$, obtained by acting on a mixture of dry sand and lead thiocyanate with phosphorous chloride, is a liquid having a specific gravity at 18° of 1.625, boiling at 260° – 270° , and decomposing at higher temperatures. It does not solidify at -20° . Its vapours burn with a brilliant flame; under certain conditions they are spontaneously inflammable. They produce violent headache, and are poisonous. This compound does not decompose on exposure to the air, and is only slowly attacked by water.

The thiocyanates of iodine, antimony, and tin have not been isolated.

β . Organic. **Acetyl Thiocyanate**, $\text{CN.S.C}^2\text{H}^3\text{O}$, is a pale yellow, strongly refracting liquid, having a pungent odour; soluble in ether and in carbon disulphide. It has a density of 1.151 at 16° ; boils with partial decomposition at 132° – 133° ; is decomposed by water, alkalis, acids, alcohol, &c., with formation of acetic and thiocyanic acids, &c.

Butyryl Thiocyanate, $\text{CN.S.C}^4\text{H}^7\text{O}$, is a strongly refracting liquid, boiling at 180° , and resembling the acetyl-compound in its other properties.

The action of the aromatic chlorides on lead thiocyanate gives rise, not to normal thiocyanates, but to isothiocyanates or thiocarbimides (p. 606).

Thiocyanates of Alcohol Radicles.

Methylene Thiocyanate, $\text{CH}^2(\text{CNS})^2$, is prepared by digesting 2 mols. potassium thiocyanate with 1 mol. methylene iodide in alcoholic solution for two or three hours on the water-bath, washing the precipitated crystals with water, and recrystallising several times from alcohol. It is easily soluble in alcohol and ether, moderately soluble in hot, nearly insoluble in cold water, and melts at 102° . On heating it for a short time with a quantity of strong nitric acid just sufficient to dissolve it, and immediately evaporating the mixture on the water-bath, removing the nitric acid by repeated evaporation with water, and treating the residuo with barium carbonate, the barium salt of methylenedisulphonic or methionic acid, $\text{CH}^2(\text{SO}^2\text{H})^2$ is formed (Julie Lermontoff, *Deut. Chem. Ges. Ber.* vii. 1282).

Ethyl Thiocyanate, $\text{C}^2\text{H}^5\text{CNS}$, obtained by the action of ethyl iodide on silver thiocyanate, boils at 141° – 142° (Meyer & Wurster, *ibid.* vi. 965).

Pseudopropyl Thiocyanate, $\text{CN.S.CH}(\text{C}^2\text{H}^5)^2$, was obtained by G. Gorlich (*Liebigs Annalen*, clxxviii. 80) as a secondary product in the preparation of artificial mustard-oil by the action of potassium thiocyanate on allyl iodide (from glycerin and phosphorus iodide), being doubtless derived from pseudopropyl iodide formed from the glycerin simultaneously with the allyl iodide. It is a liquid boiling between 152° and 163° , and having a density of 0.989 at 0° and 0.974 at 15° ; decomposed by boiling water with formation of pseudopropyl mercaptan, and completely resolved by nascent hydrogen (zinc and HCl) into the latter body and hydrogen cyanide. Strong sulphuric acid converts it into carbonyl-disulphodipseudopropyl, $\text{CO}(\text{SC}^2\text{H}^5)^2$, an ether having an offensive alliaceous odour. With hydrogen sulphide it yields persulphopseudopropylurethane, $\text{NH}^2.\text{CS.SC}^2\text{H}^5$, which crystallises from alcohol and ether in splendid rhombic laminæ, having a silky lustre and melting at 97° .

β -Hexyl Thiocyanate, $\text{CN}-\text{S}-\text{CH}(\text{C}^2\text{H}^5)^2$, is prepared by boiling equal parts of β -hexyl iodide (iii. 163) and potassium thiocyanate dissolved in the smallest possible quantity of alcohol in a reflux apparatus on the water-bath for an hour.

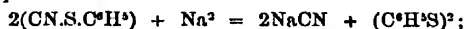
ceou
viii. 55).

Allyl Thiocyanate, $\text{CN.S.C}^3\text{H}^5$. This compound, metameric with ordinary mustard-oil ($\text{CS}=\text{N}-\text{C}^3\text{H}^5$), may be obtained by a modification of the processes employed for the preparation of the latter:—a. 1 part of ammonium thiocyanate (instead of the potassium salt) is dissolved in 3 parts of 90 per cent. of alcohol, and the solution, cooled by ice, is mixed with the theoretical quantity of allyl bromide or

iodide. On adding ice-cold water to the resulting solution, normal allyl thiocyanate separates in the form of a colourless liquid, which gradually turns yellow on exposure to light, and dissolves easily in alcohol and ether (Gerlich). β . It may also be prepared by the action of cyanogen chloride on thiocyanate of lead. This salt is left in contact for twelve hours with an anhydrous ethereal solution of cyanogen chloride; and the liquid filtered from the resulting mass is evaporated. The remaining oil consists almost wholly of allyl thiocyanate, but it cannot be purified by distillation, as it is thereby converted into the isothiocyanate, or mustard-oil (Billeter, *Deut. Chem. Ges. Ber.* viii. 464, 820). This change takes place gradually even at ordinary summer heat. By nascent hydrogen (? zinc and hydrochloric acid) the thiocyanate is resolved into hydrocyanic acid and allyl mercaptan (Gerlich). By potassium hydrosulphide it is resolved into potassium thiocyanate and allyl mercaptan; and with sodium-amalgam it yields allyl isocyanide, $C\equiv N-C^3H^3$, and sodium monosulphide (Billeter).

Phenyl Thiocyanate, $CN-S-C^6H^5$, is prepared: (1). By the action of hydrogen thiocyanide on diazobenzene sulphate; (2). By passing cyanogen chloride into alcohol in which phenylmercaptide of lead, $(C^6H^5S)^2Pb$, is suspended, the vessel being surrounded with an atmosphere of hydrogen. In the former case, the resulting phenyl thiocyanate is distilled off by heat in a stream of hydrogen, then dried and purified by fractional distillation. In the latter case, the product mixed with water yields a precipitate of nearly pure phenyl thiocyanate, which may be completely purified by two rectifications.

Phenyl thiocyanate is a colourless liquid, which gradually turns yellow; it has a density of 1.155 at 17.5° , and boils at 231° under a pressure of 706 mm. Heated to $180^\circ-200^\circ$ in a sealed tube with hydrochloric acid, it takes up hydrogen, and is resolved into phenyl mercaptan, carbon dioxide and ammonia. With potassium hydrosulphide, even at ordinary temperatures, it yields potassium thiocyanate and phenylmercaptan (Billeter, *Deut. Chem. Ges. Ber.* vii. 1753). With sodium-amalgam it reacts differently from allyl thiocyanate (p. 605), the decomposition taking place according to the equation:

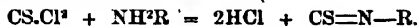


best at a temperature of 120° (Billeter, *ibid.* viii. 464).

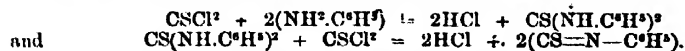
Naphthyl Thiocyanate, $CN.S.C^{10}H^7$, prepared by the action of cyanogen chloride on the lead salt of naphthyl mercaptan, $(C^{10}H^7S)^2Pb$, is a colourless substance which melts at 35° , and decomposes completely at its boiling point. By potassium hydrosulphide it is converted into potassium thiocyanate and β -naphthyl mercaptan; by strong hydrochloric acid it is resolved, by assumption of hydrogen, into β -naphthylmercaptan, carbon dioxide, and ammonia; by sodium-amalgam at $150^\circ-160^\circ$ into sodium cyanide and β -naphthyl disulphide, which forms tufts of small laminae melting at 132° (Billeter, *ibid.* viii. 463).

ISOTHIOCYANATES OR THIOCARBIMIDES, $CS=N-R$.

Alcoholic thiocarbimides (mustard-oil) are formed by the action of thiocarbonyl chloride, $CSCl^2$, on amines:



With aniline the product consists of pphenyl-thiocarbimide; if, however, the aniline is in excess, diphenyl-thiocarbimide is formed, which again may be converted into the thiocarbimide by heating with excess of thiocarbonyl chloride:



Ethylthiocarbimide is likewise easily produced by the action of $CSCl^2$ on ethylamine (Rathke, *Deut. Chem. Ges. Ber.* v. 967).

Thiocarbimides treated with alcoholic potash are converted into thiocarbamic ethers identical with those which Hofmann obtained by heating the thiocarbimides with absolute alcohol to 110° (1st Suppl. 1050). Thus a mixture of phenyl-thiocarbimide with alcoholic potash becomes hot, and deposits the compound $CS \leftarrow OC^2H^5$. Allyl-thiocarbimide (mustard-oil) is acted upon by alcoholic potash with even greater facility (R. Schiff, *ibid.* ix. 1316).

Butyl-thiocarbimides (Hofmann, *Deut. Chem. Ges. Ber.* vii. 508). The normal compound, $CS=N-CH^2-CH^2-CH^2-CH^3$, is obtained by boiling normal butylamine with ethyl alcohol and carbon disulphide, evaporating off the alcohol, and

heating the residue with solution of mercuric chloride. It boils at 167°, and yields with ammonia a slowly crystallising dibutyl-thiocarbamide which melts at 79°.

Isobutyl-thiocarbimide, $\text{CS}=\text{N}-\text{CH}_2-\text{CH}(\text{CH}_3)_2$, prepared in like manner from isobutylamine, has a density of 0.9368 at 14° , and boils at 162° ; the thiocarbimide prepared from it melts at 65.5° .

Secondary Butyl-thiocarbimide or **Methyl-ethyl-thiocarbimide**, $\text{CS}=\text{N}-\text{CH} \begin{smallmatrix} \text{OH}^{\text{H}} \\ \text{C}^{\text{H}} \end{smallmatrix}$, prepared from secondary butyl alcohol by conversion into the amine, &c., is a colourless transparent liquid having a density of 0.944 at 12°; the thiocarbimide prepared from it melts at 93.5°. This modification of butyl-thiocarbimide is the essential constituent of the oil of common scurvy-grass (p. 548).

Crotonyl-thiocarbimide, CS.N.C'H', prepared from crotonylamine (p. 538), is a colourless liquid, having a pungent odour, like that of mustard-oil, and boiling at 179°. Heated with strong aqueous ammonia, it yields a well-crystallised thiocarbamide melting at 85° (Hofmann, *loc. cit.*)

***β*-Hexyl-thiocarbimide**, prepared from *β*-hexylamino by Hofmann's process just described, is a colourless liquid having a density of 0.9253, and boiling at 197°–198°. By heating with strong sulphuric acid, it is reconverted into the amine, with separation of sulphur (Uppenkamp, *Ber.* viii. 55).

Phenyl-thiocarbimide. On the reaction of this compound with *aldehyde ammonia*, see p. 399 of this volume.

Thiocarbimides containing Aromatic Acid Radicles (Miquel, *Ann. Chim. Phys.* [5], xi. 289).

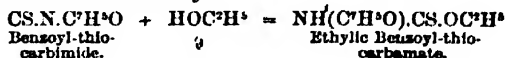
* These compounds, as already observed, are formed by the action of the corresponding acid chlorides on lead thiocyanate; the acid chlorides of the fatty series under similar circumstances produce normal acid thiocyanates (p. 605).

Benzoyl-thiocarbimide, $\text{CS}=\text{N}-\text{C}^6\text{H}_5\text{O}$, is a strongly refracting liquid, smelling like bitter almonds, and having a density of 1.197 at 16° . Heated to 200° it decomposes, giving off torrents of carbon oxysulphide. It dissolves in ether, carbon disulphide, and chloroform, and unites with alcohol, forming an ether. By boiling water it is completely resolved into benzamide and carbon oxysulphide:



Ammonia, either gaseous or in aqueous solution, converts benzoyl-thiocarbimide into monobenzoyl-thiocarbamide, $\text{NH}_2\text{CS.NH(C}_6\text{H}_5\text{O)}$. *Amines* convert it into thiocarbamides containing benzoyl and an alcohol radicle, e.g. $\text{NH(C}_6\text{H}_5\text{O).CS.NH(C}_6\text{H}_5\text{O)}$ (p. 400).

Benzoyl-thiocarbimide unites at ordinary temperatures with *alcohols* and *phenols*, forming thiocarbamic ethers, e.g.:



With ethyl- and methyl-alcohol the combination takes place readily, but the higher alcohols and the phenols require to remain in contact with the thiocarbimide for several weeks or months before complete union is effected.

The thiocarbamic ethers thus formed are easily decomposed by heat or by the action of acids or alkalis; they are desulphurised by the oxides of silver and mercury, forming the corresponding ethers of carbamic acid. An alcoholic solution of potash or soda forms with these thiocarbamates, crystalline compounds identical with the potassium or sodium substitution-products obtained by the action of potassium or sodium methylate or ethylate on benzoyl-thiocarbimide.

Methylic Benzoyl-thiocarbamate, $\text{NH}(\text{C}_2\text{H}_5)\text{CS.OCH}_3$, is deposited from a boiling alcoholic solution in silky needles melting at 97° , decomposing at 106° . It is slightly soluble in water, and dissolves easily in ether and in methyl and ethyl alcohol. Its solution reduces silver, bismuth, and copper salts in the cold, and gives with mercuric chloride a white precipitate, and with gold chloride a yellow precipitate.

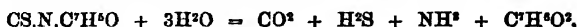
Methylic Sodium-benzoyl-thiocarbamate, $\text{CS} \begin{matrix} \text{NNaC}^{\text{H}}\text{O} \\ \text{OCH}_3 \end{matrix}$, is obtained in small crystals by the action of alcoholic soda-solution on the preceding compound, or by the action of sodium methylate on an ethereal solution of benzoyl-thiocarbamide.

Ethylc Benzoyl-thiocarbamate described by Loessner (*J. pr. Chem.* [2], x. 235) as

benzoyl-ethyl-oxythiocarbamic acid, is a crystalline body, slightly soluble in water, it melting at 73°-74°, and decomposing at 85°.

Amylio Benzoyl-thiocarbamate is a syrupy liquid. *Phenylis Benzoyl-thiocarbamate* is a slightly yellow crystalline body, insoluble in water, very soluble in alcohol and ether. It melts at 93°, and decomposes at a slightly higher temperature.

Metabenzoyl-thiocarbimide.—This name is given to a polymeric modification of benzoyl-thiocarbimide, which is deposited in the form of an orange-yellow substance, when recently distilled benzoyl-thiocarbimide is left at rest for some weeks, or frequently after a few hours. When purified by strong pressure and repeated treatment with boiling water and strong alcohol, and dried at 100°, it forms a yellow, amorphous, tasteless powder, having a faint aromatic odour. It melts at about 160° to a colourless liquid which remains for a long time in a state of surfusion. It is decomposed by the fixed alkalis, but not by ammonia. By water at 200° it is resolved into carbon dioxide, hydrogen sulphide, ammonia and benzoic acid:



Nitric acid dissolves and decomposes it, forming benzoic acid. By aromatic monamines it is converted, like benzoyl-thiocarbimide, into disubstituted thiocarbamides containing benzoyl.

Salicyl-thiocarbimide, $\text{CS.N.C}^7\text{H}^5\text{O}^2$, is formed by the action of salicyl chloride on thiocyanate of lead, but has not been obtained in the pure state, on account of the difficulty of freeing the salicyl chloride from viscous products and phosphorus oxychloride. The magma produced by the reaction yields to ether the whole of the thiocarbimide; and on expelling the ether by heat or by exposure for a short time in a vacuum, a thick brown syrup is left which cannot be distilled, even under reduced pressure, without decomposing and giving off carbon oxysulphide. That it consists in great part of salicyl-thiocarbimide is shown however by its reactions: thus with water at 100° it yields salicylamide and carbon oxysulphide; ammonia converts it into salicyl-thiocarbamide; and with aniline it likewise yields a thiocarbamide.

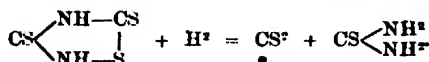
Salicyl-thiocarbimide is isomeric, if not identical, with the thiocarbamidobenzoic acid (p. 269) which Rathke & Schaefer obtained by the action of thiocarbonyl chloride on amidobenzoic acid (Miquel).

Dithiocyanic acid, $\text{C}^7\text{N}^2\text{S}^2\text{H}^2$. This polymeride of thiocyanic acid is formed from perthiocyanic acid by the action of potash either in alcoholic or in aqueous solution. In the former case the potassium salt of dithionic acid separates out, and the liberated sulphur remains in solution; in the latter, the contrary is the case. *Potassium dithiocyanate*, $\text{C}^7\text{N}^2\text{S}^2\text{K}^2 + \text{H}^2\text{O}$, crystallises in monoclinic prisms insoluble in alcohol, freely soluble in water, and melting at 170°. On treating it with sulphuric acid, free dithiocyanic acid gradually separates in the form of a dark yellow amorphous body, which may be dissolved by alcohol or by hot water, but suffers decomposition in the latter case. The *barium salt*, $\text{C}^7\text{N}^2\text{S}^2\text{Ba} + 2\text{H}^2\text{O}$, is easily soluble in water and crystallises in rhombic prisms. The *copper-salt* is a brown-red powder; the *lead* and *silver salts* are lemon-yellow powders: all three insoluble in water. A *silver-potassium salt*, $\text{C}^7\text{N}^2\text{S}^2\text{AgK}$, may be obtained in the form of pale yellow scales. The *ethylic ether*, $\text{C}^7\text{N}^2\text{S}^2(\text{C}^2\text{H}^5)^2$, prepared from the potassium salt by means of ethyl bromide, is a thickish red-brown liquid not volatile without decomposition (A. Fleischer, *Liebig's Annalen*, clxxix. 204).

Perthiocyanic acid, $\text{C}^7\text{N}^2\text{S}^3\text{H}^2$ (iv. 378; 2nd Suppl. 899). The preparation and properties of this body have lately been studied by R. W. Atkinson (*Chem. Soc. Jour.* 1877, ii. 255). He finds that the yellow precipitate obtained in the usual way by decomposing potassium thiocyanate with hydrochloric acid differs in composition accordingly as it is washed with hot or with cold water, and that to obtain a pure product, the acid must be crystallised from hot water. It then separates in long and often curved woolly tufts, which, after drying in the air and pressure between bibulous paper, do not lose more than a trace of moisture when heated to 120°. By treating the alcoholic solution of the acid with excess of silver nitrate, a yellow precipitate was obtained having the composition $\text{C}^7\text{N}^2\text{S}^3\text{Ag}^2$, and with smaller quantities of silver nitrate, precipitates were formed approximating to the formula $\text{C}^7\text{N}^2\text{S}^3\text{AgH}$. When the diargentate salt is boiled with water, effervescence takes place, and a black precipitate is formed, the composition of which has not been determined. The yellow precipitate formed by mercurous nitrate in a solution of perthiocyanic acid, has nearly the composition $\text{C}^7\text{N}^2\text{S}^3\text{Hg}^2$, and is not perceptibly decomposed by heating.

The formation of the diargentate and dimercurose salts is easily accounted for, if we adopt the formula of perthiocyanic acid proposed by Glutz (*Deut. Chem. Ges. Ber.*

Eq. 343), viz. $\text{CS} \begin{array}{c} \text{NH}-\text{CS} \\ | \\ \text{NH}-\text{S} \end{array}$, which is analogous to that of parabanic acid, $\text{CO} \begin{array}{c} \text{NH}-\text{CO} \\ | \\ \text{NH}-\text{O} \end{array}$. The formula is likewise in accordance with the formation of thiocarbamide and carbon disulphide by the action of nascent hydrogen (tin and HCl) on the acid:



The following reactions of perthiocyanic acid, examined by J. Ponomareff (*Compt. rend.* lxxix. 1335), point to a different formula of the acid, viz. $\text{C}^2\text{N}^2\text{S}^2\text{H}$, as proposed by Laurent a. Gerhardt.

1. Phosphorus pentachloride begins to act on the acid at 125° , a red-brown pungent oil distilling over. At about 170° large shining laminae sublime on the sides of the retort, consisting of solid cyanogen chloride, $\text{C}^2\text{N}^2\text{Cl}^2$, and a distillate is obtained containing phosphorus sulphochloride, PSCl^2 , together with sulphur chloride, S^2Cl^2 , and phosphorus trichloride. The formation of these products may be represented by the following equation:



2. Perthiocyanic acid, heated to 150° – 160° in a sealed tube with excess of ammonia, yields ammonium thiocyanate, which may be expelled by evaporating the product with water, and needle-shaped crystals, which may be recrystallised from boiling water, and are slightly soluble in cold water, but insoluble in alcohol and ether. These crystals partly sublime when gently heated, and give off ammonia at higher temperatures. They have the composition $\text{C}^2\text{H}^4\text{N}^2\text{S}$, and react like melamine thiocyanate, $\text{C}^2\text{N}^4(\text{NH}^2)^2\text{CNSH}$ (p. 604), being resolved by potash into melamine and potassium thiocyanate.

Acetyl-perthiocyanic acid, $\text{C}^2\text{H}(\text{C}^2\text{H}^2\text{O})\text{N}^2\text{S}^2$ (Nencki a. Leppert, *Deut. Chem. Ges. Ber.* vi. 902).—This acid is formed, as already observed (p. 603), by heating ammonium thiocyanate with acetic anhydride or acetic acid. In the former case, the heat should not be allowed to rise above 80° . The resulting liquid solidifies on cooling to a crystalline mass, which when treated with an equal volume of water, yields a copious granular precipitate of acetyl-perthiocyanic acid. The product may be washed with cold water and recrystallised from 90 per cent. alcohol. When acetic acid is used in the preparation, a small quantity of a reddish crystalline body is also formed, from which the acetyl-perthiocyanic acid may be separated by solution in dilute ammonia and precipitation with hydrochloric acid.

According to De Clermont (*Compt. rend.* lxxxiii. 1103), acetyl-perthiocyanic acid may also be prepared by boiling acetic anhydride with perthiocyanic acid in a reflux apparatus.

Acetyl-perthiocyanic acid crystallises from alcohol in yellow needles. It dissolves in alcohol and ether more readily than in boiling water. The solutions have an acid reaction, and yield with the greater number of metals, amorphous insoluble precipitates. It dissolves easily in dilute ammonia, and separates unaltered on addition of a stronger acid. By the fixed alkalis, on the contrary, it is rapidly decomposed, the resulting solutions, when acidulated and warmed, giving off acetic acid and hydrogen sulphide.

The only metallic acetyl-perthiocyanate which has been obtained of constant composition is the copper-salt. On adding cupric sulphate to a solution of acetyl-perthiocyanic acid in dilute ammonia, an olive-green amorphous precipitate is formed which quickly turns red, and, according to the results of copper and nitrogen determinations, appears to have the composition $2\text{Cu}[\text{C}^2\text{H}(\text{C}^2\text{H}^2\text{O})\text{N}^2\text{S}^2]^2 + \text{CuO}$.

By the action of reducing agents (iron filings and acetic acid, or tin and hydrochloric acid) acetyl-perthiocyanic acid is converted into thiocarbamide.

CYANIDE OF ACETYL, $\text{C}^2\text{H}^2\text{O}.\text{CN}$. In preparing this compound, Hübner's method of heating acetyl chloride with silvercyanide, Fileti (*Gazz. chim. ital.* v. 391) obtained a first fraction containing a small quantity of acetyl chloride, a second portion boiling at 93° , and consisting of the cyanide, and a third fraction from about 93° – 200° . The first fraction, when allowed to evaporate at the ordinary temperature, left a colourless crystalline residue, which, after being purified by crystallisation from alcohol, melted at 120° , and gave off ammonia when heated with a solution of potash. The portion boiling up to 200° also deposits crystals when cooled by a mixture of

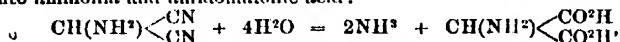
ice and salt. This new compound may perhaps be a polymeride of acetyl cyanide, produced by the action of heat; or, less probably, the nitril of pyruvic acid.

CYANIDE OF HYDROGEN, CNH. *Spontaneous Alteration.*—It is well known that anhydrous hydrocyanic acid sometimes suffers decomposition in a very short time, whereas at other times it may be kept for months without change. This difference arises from the calcium chloride used in drying the acid. If the calcium chloride is neutral, the acid obtained will be pure; but if the chloride is alkaline, as it is when ignited in the open air, the acid rapidly decomposes. The explanation of this fact is that on the contact of the acid with the lime contained in the ignited calcium chloride, calcium cyanide is formed; this, with the water contained in the hydrocyanic acid, gives rise to the formation of calcium formate and ammonia, and it is known that a trace of ammonia is sufficient to determine the decomposition of the anhydrous hydrocyanic acid.

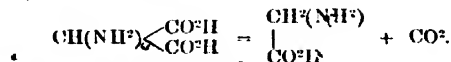
If some pure anhydrous acid be heated in a sealed tube for four or five hours, the liquid solidifies to a compact black mass. On opening the tube, there is no evolution of gas, and the black substance has the total weight of the acid employed, and the same centesimal composition. On heating it in a tube open at one end, ammonium cyanide is at first formed, then cyanogen, and a carbonaceous residue is left; but it may be heated to 50° without alteration. On treating the black substance with ether, a crystallisable body is obtained. A similar decomposition takes place on heating the anhydrous acid with alcohol or ether (J. de Girard, *Compt. rend.* lxxxiii. 344).

Polymerisation.—The polymeride of hydrocyanic acid, $C^2N^2H^2$, which Lange obtained by the action of hydrocyanic acid on epichlorhydrin (2nd Suppl. 411), has been further examined by R. Wippermann (*Deut. Chem. Ges. Ber.* vii. 767). This body is always formed when aqueous hydrocyanic acid, either dilute or concentrated, is kept for a week in contact with a solution of caustic alkali or alkaline carbonate: azulmic acid is formed at the same time. The trihydrocyanic acid is extracted from the product by ether, and after evaporation of the ether, purified by recrystallisation from boiling water. It forms crystals, apparently triclinic, exhibiting the combination $0P \cdot \infty P \cdot \infty P \infty$, and tabular from predominance of $0P$; they decompose partially at a temperature below their melting point (180°), and when heated above that point, undergo explosive decomposition, with emission of hydrocyanic acid.

The constitution of this compound is inferred from its reaction with barium peroxide and with chlorine, both of which act upon it with aid of heat, in such a manner that it is resolved, with addition of water, into glycocine (amidacetic acid), carbon dioxide, and ammonia. Hence Wippermann concludes that trihydrocyanic acid has the constitution of amidomalo-nitril, $CH(NH^2) \begin{smallmatrix} \text{CN} \\ \diagup \end{smallmatrix} \begin{smallmatrix} \text{CN} \\ \diagdown \end{smallmatrix}$, which is resolved by assumption of water into ammonia and amidomalonic acid:

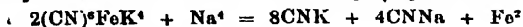


this acid being, however, immediately resolved into amidacetic acid and carbon dioxide:



CYANIDES, METALLIC. These compounds (e.g. potassium or zinc cyanide) are decomposed, with evolution of hydrogen cyanide, by passing a stream of an indifferent gas (CO^2 , H, or air) through their aqueous solutions (Naudin a. de Montholon, *Compt. rend.* lxxxiii. 345).

A pure solution of alkali-metal cyanide is easily obtained by fusing dehydrated potassium ferrocyanide with sodium, and lixiviating the product:



(Erlenmeyer, *Deut. Chem. Ges. Ber.* ix. 1840).

Potassium cyanide, treated in aqueous solution with hydrogen sulphide, yields chrysæan, $C^2H^2N^2S^2$ (p. 463). With calcium hypochlorite, it yields calcium dicyanate (fulminate), together with potassium chloride (Ainno, *J. Pharm. Chim.* [4], xxii. 401).

Mercuric Cyanide. *Compounds with the Earth-metals.*—The following bodies, represented by the formula $M^2Cl^2 \cdot 6Hg(CN)^2 + 16H^2O$ (where M = Ca, La, Di, Y, and Er), are obtained by crystallisation from a solution of mercuric cyanide with an excess of the respective chlorides. They are all very soluble, and lose their water of crystallisation at 100°, and over oil of vitriol. They crystallise only from solutions containing an excess of the chloride. *Cerium salt*: tough, asbestos-like needles. *Lanthanum salt*: colourless, silky needles. *Didymium salt*: rose-coloured, elastic needles. *Yttrium salt*: colourless, radiate, and well-defined prisms, losing 3 mols. H^2O over

oil of vitriol. *Erbium salt*: reddish, resembling the preceding (J. E. Ahlen, *Bull. Soc. Chim.* [2], xxvii. 365).

Thallium Cyanides (Fronmüller, *Deut. Chem. Ges. Ber.* vii. 1178. *Inaugural-dissertation*, Marburg, 1876). *Thallious cyanide*, TlCN , is prepared by mixing a solution of thallious sulphate saturated at the boiling heat with a quantity of saturated baryta-water sufficient to precipitate the whole of the sulphuric acid, and adding to the cold filtrate, first concentrated hydrocyanic acid, and then a large quantity of alcohol, and as much ether as will dissolve in the liquid. An amorphous white precipitate is thus formed, which is quickly washed with ether-alcohol, and dried in a vacuum.

Thallious cyanide crystallises from a hot concentrated solution in small glistening plates; it smells strongly of hydrocyanic acid, and is readily soluble in water; 100 parts of water at 28.5° dissolve 16.8 parts. When heated, it melts and decomposes a non-inflammable gas being given off, and metallic thallium mixed with carbonaceous matter being left behind. The aqueous solution has an alkaline reaction, and is readily decomposed by carbonic acid. When the solution is heated in a sealed tube for some time, the salt is completely decomposed into ammonia and thallium formate.

Thallium-silver Cyanide, $\text{TlCN} \cdot \text{AgCN}$, is prepared by adding silver cyanide to a solution of thallious cyanide or of thallious oxide mixed with hydrocyanic acid, and evaporating the resulting solution. It forms small dazzling white crystals which are decomposed by strong acids (nitric acid) into silver cyanide and a thallium salt.

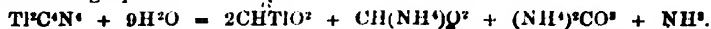
Thallium-zinc Cyanide, $2\text{TlCN} \cdot \text{Zn}(\text{CN})_2$, prepared like the silver-compound, forms colourless hemihedral crystals of the regular system, permanent in the air, easily soluble in water, 100 parts of water dissolving 29.67 parts of it at 31° , 15.17 pts. at 14.0° , 8.67 parts at 0° .

Thallos-mercuric Cyanide, $2\text{TlCN} \cdot \text{Hg}(\text{CN})_2$, forms colourless monometric crystals, of which 100 parts of water dissolve 10.28 pts. at 10° , and 7.9 pts. at 1° .

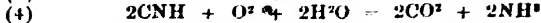
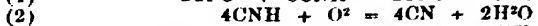
Thallos-cobaltic Cyanide, $\text{Co}^2\text{Tl}^2(\text{CN})^{12} = 6\text{TlCN} \cdot \text{Co}^2(\text{CN})_6$, prepared by heating thallious cyanide on the water-bath for a considerable time with cobaltous oxide and hydrocyanic acid, crystallises in faintly yellowish crusts. 100 parts of water dissolve 10.04 pts. of the salt at 19.5° ; 5.86 pts. at 9.5° ; 3.6 pts. at 0° . It is decomposed by nitric and by dilute sulphuric acid, with separation of thallium salt and formation of hydrocobaltic acid. With salts of the heavy metals it forms coloured precipitates.

Thallos-thallic Cyanide, $\text{TlCN} \cdot \text{Ti}(\text{CN})_3$, prepared by treating moist thallic oxide with moderately concentrated hydrocyanic acid, and evaporating the solution, separates partly in tabular crystals, partly in double pyramids belonging to the rhombic system, $P : P$ in the lateral edges = 126.8° ; in the terminal edges, 90.3° and 100.55° . 100 pts. of water dissolve 27.31 pts. of the salt at 30° ; 15.29 pts. at 12° , 9.75 pts. at 0° .

Thallosothallic cyanide is unstable in aqueous solution, being resolved into thallious formate, ammonium formate, ammonium carbonate and ammonia, according to the following equation:



Mineral acids decompose it, with evolution of hydrocyanic acid; potash throws down thallic hydrate, leaving thallious oxide in solution; hydrogen sulphide precipitates part of the thallium as black thallious sulphide, Ti^2S ; silver nitrate throws down silver cyanide; potassium iodide and zinc iodide throw down thallious iodide. These reactions show that the formula of the thallium cyanide under consideration is really $\text{TlCN} \cdot \text{Ti}(\text{CN})_3$, and not $\text{Ti}(\text{CN})_3$, and this conclusion is further established by the fact that the solution of thallic oxide is attended with evolution of carbon dioxide, the course of the reaction being represented by the following equations:



On Cyanide of Thallium and Platinum, see p. 618.

FERROCYANIDES, $\text{R}^2\text{Fe}^2(\text{CN})_6$.

The black matter left in the calcination of pure dry potassium ferrocyanide consists of a mixture of metallic iron carburised to about the same extent as pig-iron, with magnetic oxide of iron and uncombined carbon, as exhibited in the following table:

Metallic iron.	Iron as magnetic oxide.	Carbon uncombined.	Carbon combined with iron.
32.05	27.56	27.46	1.17
Carbon as cyanogen.	Potassium.	Nitrogen.	Oxygen.
0.24	0.81	0.23	10.50

(A. Terrell, *Compt. rend.* lxxxii. 455).

The following ferrocyanides, obtained by precipitating a solution of the potassium salt with solutions of the several metals, have been examined by Wyruboff (*Ann. Chim. Phys.* [5], viii. 444).* Compare 2nd Suppl. 412.

(1.) *Containing only a Univalent Metal:*

Silver salt. $\text{Ag}^+\text{Fe}(\text{CN})^6 + \text{H}_2\text{O}$. White very deliquescent salt, converted by ammonia into the compound, $\text{Ag}^+\text{Fe}(\text{CN})^6(\text{NH}_4)^2\text{O}^2$.

(2.) *Containing Bivalent Metals:*

Copper salts. $\text{Cu}^2\text{Fe}(\text{CN})^6 + 10\text{H}_2\text{O}$ (Hatchett's brown); $(\text{Cu}^2)^2\text{K}^2(\text{CN})^4\text{K}^+\text{Fe}(\text{CN})^6 + 12\text{H}_2\text{O}$ (dark brown); and $\text{CuKFe}(\text{CN})^6 + \text{H}_2\text{O}$? (red-brown). The mother-liquor of the first salt also contains a salt having the composition $\text{Cu}^2\text{K}^3\text{Fe}(\text{CN})^6 + 6\text{H}_2\text{O}$.

Bong (*Compt. rend.* lxxx. 659) describes a red copper-compound $\text{FeCu}(\text{CN})^6 \cdot 4\text{H}_2\text{O}$ (?), prepared by adding potassium cyanide to an acid solution of a copper-salt, till the rose-colour at first produced has disappeared, and then adding an acid iron solution. From the resulting precipitates, which contain prussian blue, ammonium carbonate extracts copper cyanide and a colouring substance which may be separated from the alkaline solution by an acid. This last precipitate is freed from copper by hydrogen sulphide, and the latter is removed by lead carbonate. The resulting purple solution from which the colouring matter cannot be removed by iron or lead salts, but is completely precipitated by zinc, copper, and mercury salts, yields with cupric acetate a compound said to have the formula above given. The solution of this colouring matter, after being freed from copper, yields an ammonium salt which dries up in a vacuum to a red mass. It is not decomposed by boiling aqueous alkalis, or by sulphurous acid or hydrogen sulphide; but nitric acid, chlorine, and mercuric oxide destroy it quickly.

Cobalt salts. $\text{Co}^2\text{Fe}(\text{CN})^6 \cdot \text{K}^+\text{Fe}(\text{CN})^6$ (dark violet); $2\text{Co}^2\text{Fe}(\text{CN})^6 \cdot \text{Co}^+\text{K}^+\text{Fe}(\text{CN})^6 + 14\text{H}_2\text{O}$? (pale-red); $\text{Co}^2\text{Fe}(\text{CN})^6 + 7\text{H}_2\text{O}$ (emerald green); and $2\text{Co}^2\text{Fe}(\text{CN})^6 \cdot \text{Co}^+\text{K}^+\text{Fe}(\text{CN})^6$? (grey-green). The first of these salts is obtained by precipitation with potassium ferrocyanide; the second in like manner with excess of the latter; the third and fourth with hydrogen ferrocyanide; the fourth with excess of the latter.

Nickel salts. $\text{Ni}^2\text{Fe}(\text{CN})^6 \cdot \text{K}^+\text{Fe}(\text{CN})^6 + 6\text{H}_2\text{O}$ (light rose-coloured), from yellow prussiate and nickel solution; $\text{Ni}^2\text{K}^2[\text{Fe}(\text{CN})^6]^2 \cdot \text{K}^+\text{Fe}(\text{CN})^6 + 13\text{H}_2\text{O}$? (light-green), prepared with excess of yellow prussiate; $\text{Ni}^2\text{Fe}(\text{CN})^6 + 14\text{H}_2\text{O}$ or $11\text{H}_2\text{O}$, with hydroferrocyanic acid; combining with $14\text{H}_2\text{O}$ when precipitated in the cold; with $11\text{H}_2\text{O}$ at boiling heat.

Zinc salts. $3\text{Zn}^2\text{Fe}^2(\text{CN})^6 \cdot \text{K}^+\text{Fe}(\text{CN})^6 + 12\text{H}_2\text{O}$ and $\text{Zn}^2\text{Fe}(\text{CN})^6 + 4\text{H}_2\text{O}$, are white precipitates, the first formed with yellow prussiate, the second with hydroferrocyanic acid. There is also a zinc ferrocyanide, $\text{Zn}^2\text{Fe}(\text{CN})^6 + 6\text{H}_2\text{O}$, obtained by treating the ferrieyanide with ammonia.

Cadmium salt. $\text{Cd}^2\text{K}^+\text{Fe}(\text{CN})^6 + 11\text{H}_2\text{O}$? Pale yellow; converted by ammonia into red crystals, $\text{Cd}^2[\text{Fe}(\text{CN})^6]^2 \cdot 2(\text{NH}_4)^2\text{O}$? soluble in ammonia.

(3.) *Containing Trivalent Metals:*

Iron. **Ironide** occurs in the salts $\text{Ce}^4\text{KFe}(\text{CN})^6 + 4\text{H}_2\text{O}$, and $\text{Ce}^4.3\text{Fe}(\text{CN})^6 + 10\text{H}_2\text{O}$, both of which are white; the first is prepared with potassium ferrocyanide, the second with hydrogen ferrocyanide.

Didymiopotassic Ferrocyanide. $\text{Di}^{\text{III}}\text{KFe}(\text{CN})^6$, crystallises with $2\text{H}_2\text{O}$ (Wyruboff), with $4\text{H}_2\text{O}$ (Cleve).

Lanthano-potassic Ferrocyanide. $\text{La}^{\text{III}}\text{K}^+\text{Fe}(\text{CN})^6 + 4\text{H}_2\text{O}$, is prepared like the corresponding cerium salt.

Yttrio-potassic Ferrocyanide. $\text{Y}^{\text{III}}\text{K}^+\text{Fe}(\text{CN})^6 + 2\text{H}_2\text{O}$, is a white powder (Cleve a. Hoeglund).

Aluminium Ferrocyanide. $\text{Al}^3.3\text{Fe}(\text{CN})^6 + 17\text{H}_2\text{O}$, (?) is a bluish white salt slightly soluble in water.

* Some of Wyruboff's formulae are anomalous, and probably founded on defective analyses.

Ferrocyanide, $(\text{Bi}-\text{Bi})^{\text{v}} \cdot \text{Fe}(\text{CN})^{\text{v}} + 5\text{H}^2\text{O}$, is obtained by precipitation with hydrogen ferrocyanide; *bismuth potassic ferrocyanide*, $\text{Bi}^{\text{v}} \cdot \text{K} \cdot \text{Fe}(\text{CN})^{\text{v}} + 4\text{H}^2\text{O}$, with potassium ferrocyanide (Wyruboff).

Muir (*Chem. Soc. J.* 1877, i. 654), by adding a cold (previously boiled) solution of bismuth nitrate to a solution of potassium ferrocyanide in boiled water, obtained a white precipitate, which after drying over sulphuric acid in a vacuum, exhibited the composition $\text{Bi}^{\text{v}} \cdot 5\text{Fe}(\text{CN})^{\text{v}}$ [bismuth quinquivalent]. This salt becomes slightly coloured even when dried in the exsiccator as above, and at 100° it gives off hydrocyanic acid, and becomes more or less deeply covered with a blue film; it becomes darker in colour at 150° , and is completely decomposed at 180° . By warming with very dilute nitric acid it is converted into the ferricyanide (p. 615). The same change takes place more or less completely when the ferrocyanide suspended in water, cold or boiling, is subjected to the action of bromine or chlorine, and in presence of cold or hot solutions of caustic soda, the ferrocyanide is completely decomposed by bromine or chlorine, the whole of the bismuth and iron contained in it being precipitated (Muir, *ibid.* ii. 44).

(4.) Containing Quadrivalent Metals:

Tin salts. $\text{Sn}^{\text{iv}} \cdot \text{K}^{\text{v}} \cdot 11\text{Fe}(\text{CN})^{\text{v}} + 230\text{H}^2\text{O}$, is a white mass (Atterberg, *Bull. Soc. Chim.* [2], xxiv. 355). According to Wyruboff, stannous chloride and yellow prussiate, yield a dark grey salt, $\text{Sn}^{\text{iv}} \cdot 2\text{Fe}(\text{CN})^{\text{v}} + 18\frac{1}{2}\text{H}^2\text{O}$; stannic chloride and yellow prussiate a white salt, $\text{Sn}^{\text{iv}} \cdot 4\text{Fe}(\text{CN})^{\text{v}} + 4\text{H}^2\text{O}$; stannous chloride and red prussiate, a bluish-white salt, $\text{Sn}^{\text{iv}} \cdot 4\text{Fe}(\text{CN})^{\text{v}} + 25\text{H}^2\text{O}$. These formulæ are very improbable.

Titanium salts. $\frac{3\text{TiO}}{\text{K}^{\text{v}}} \cdot 2\text{Fe}(\text{CN})^{\text{v}} + 23\text{H}^2\text{O}$ and $\frac{11\text{TiO}}{\text{K}^{\text{v}}} \cdot 6\text{Fe}(\text{CN})^{\text{v}} + 110\text{H}^2\text{O}$ are precipitates, the first yellowish-brown, the second dark brown (Atterberg).

Wyruboff describes three titanic ferrocyanides represented by the anomalous formulæ $\text{Ti}^{\text{iv}} \cdot \text{K}^{\text{v}} \cdot 2\text{Fe}(\text{CN})^{\text{v}} + 11\text{H}^2\text{O}$; $\text{Ti}^{\text{iv}} \cdot 11\text{Fe}(\text{CN})^{\text{v}} \cdot \text{K}^{\text{v}} \cdot \text{Fe}(\text{CN})^{\text{v}} + 43\text{H}^2\text{O}$; and $\text{Ti}^{\text{iv}} \cdot 2\text{Fe}(\text{CN})^{\text{v}} + 25\text{H}^2\text{O}$, prepared with yellow prussiate and titanic oxychloride, the first with excess of yellow prussiate, the second with a moderate excess, and the third with a large excess of titanic oxychloride. They are all brown precipitates.

(5.) Containing Quinquivalent Metals:

Vanadium Ferrocyanide, $\frac{5\text{VO}}{\text{K}^{\text{v}}} \cdot 4\text{Fe}(\text{CN})^{\text{v}} + 60\text{H}^2\text{O}$, is a greenish precipitate formed with excess of potassium ferrocyanide; the salt $2\text{VO} \cdot \text{Fe}(\text{CN})^{\text{v}} + 11\text{H}^2\text{O}$, on the other hand, is a yellowish-green pulverulent precipitate formed in presence of excess of potassium vanadate (Atterberg).

Wyruboff describes the compound $\text{VK}^{\text{v}} \cdot 6\text{Fe}(\text{CN})^{\text{v}}$ as a light green salt, slightly soluble in water. Atterberg is of opinion that Wyruboff's calculation is vitiated by non-attention to the fact that vanadic acid is reduced by potassium ferrocyanide to vanadium dioxide.

Niobium Ferrocyanide, $\frac{5\text{NbO}}{\text{K}^{\text{v}}} \cdot 6\text{Fe}(\text{CN})^{\text{v}} + 10\text{H}^2\text{O}$, is a brownish salt (Atterberg).

Wyruboff describes the salts $\text{Nb}^{\text{v}} \cdot \text{K}^{\text{v}} \cdot 2\text{Fe}(\text{CN})^{\text{v}} + 67\text{H}^2\text{O}$ and $\text{Nb}^{\text{v}} \cdot \text{K}^{\text{v}} \cdot \text{Fe}(\text{CN})^{\text{v}} + 39\text{H}^2\text{O}$, the latter prepared from potassium niobate and yellow prussiate, with subsequent addition of hydrochloric acid, the former with a large excess of yellow prussiate.

(6.) Containing Sexvalent Metals:

Molybdenum salts, $\frac{3\text{MoO}_2}{\text{K}^{\text{v}}} \cdot 2\text{Fe}(\text{CN})^{\text{v}} \cdot 2\text{MoO}_2 + 20\text{H}^2\text{O}$, is a brown precipitate. A similar salt, $\frac{\text{MoO}_2}{\text{K}^{\text{v}}} \cdot 2\text{Fe}(\text{CN})^{\text{v}} \cdot 2\text{MoO}_2 + 12\text{H}^2\text{O}$, obtained with excess of potassium ferrocyanide, is a brownish powder soluble in water (Atterberg).

Wyruboff describes a dark brown salt, $\text{Mo}^{\text{v}} \cdot \text{Fe}(\text{CN})^{\text{v}} \cdot \text{K}^{\text{v}} \cdot \text{Fe}(\text{CN})^{\text{v}} + 40\text{H}^2\text{O}$; a lighter brown salt, $\text{Mo}^{\text{v}} \cdot \text{Fe}(\text{CN})^{\text{v}} + 20\text{H}^2\text{O}$; a yellow-brown salt, $\text{Mo}^{\text{v}} \cdot \text{Fe}(\text{CN})^{\text{v}} + 8\text{H}^2\text{O}$; and a light brown salt, $\text{Mo}^{\text{v}} \cdot \text{Fe}(\text{CN})^{\text{v}} + 14\text{H}^2\text{O}$. The first is obtained with yellow prussiate and acid ammonium molybdate; the second with yellow prussiate and molybdous chloride or a molybdic oxy-salt; the third with hydroferrocyanic acid and ammonium molybdate; the fourth in like manner, but with excess of hydroferrocyanic acid. Of these salts the fourth is very soluble in water, but may be precipitated from the aqueous solution by alcohol. They are all, except the third, inclined to decompose in contact with the air. They all dissolve in ammonia, and are precipitated therefrom by acids; in this way, the third salt may be prepared from the fourth. The determination of the iron and of the molybdenum in these salts is difficult, but may be effected by oxidising the salt with nitric acid and adding ammonia, which precipitates the iron; or the molybdenum may be estimated volumetrically in presence of the

iron by Pisaní's method (reduction with zinc and hydrochloric acid, and titration with permanganic acid), whereby first the molybdenum and then the iron is oxidised (this mode of titration cannot be exact; *Jahresb. f. Chem.* 1876, 313). According to Atterberg, the analysis of molybdenum ferrocyanide must be effected by fusion with an alkaline carbonate, the separation of the iron and molybdenum by ammonia, as in Wyruboff's method, not being complete.

Tungsten Ferrocyanides. $W^2K^2Fe(CN)^6 + 20H^2O$, and $W^2K.Fe(CN)^6 + 7H^2O$ (according to Wyruboff), are red-brown precipitates.

Uranium Ferrocyanide, $\frac{3UO_2}{K_2} \cdot 2Fe(CN)^6 + xH^2O$, is a brownish powder. If an excess of potassium ferrocyanide be used in the preparation, a salt is formed having the composition $\frac{5UO_2}{K_6} \cdot 4Fe(CN)^6 + 60H^2O$ (Skraup). See also Wyruboff (*loc. cit.*)

Iron Ferrocyanides. Prussian Blues. [Skraup, *Wien. Akad. Ber.* lxxiv. (2 Abth.) Juniheft, 1876]. Soluble blue is obtained: α . From ferric chloride and potassium ferrocyanide, the solutions, in molecular proportion, $2K^2Fe(CN)^6 : Fe^2Cl^6$, being mixed rapidly, and in such a manner that no excess of either shall be present at any moment during the operation. This is effected by the use of titrated solutions brought to the same volume, and poured simultaneously and with constant stirring into a third vessel. The resulting precipitate is purified by washing it on a filter with a little water, then dried in a vacuum over sulphuric acid.

The compound thus obtained has the composition $(Fe^2)^4(K^2 \cdot 2Fe(CN)^6) + 3\frac{1}{2}H^2O$. It dissolves completely in cold water, forming a solution of a pure blue colour, but by boiling with water it is completely decomposed, with separation of a dingy yellow precipitate. The blue solution forms a blue precipitate with various bodies (potassium iodide solution containing excess of iodine, mineral acids, and salts of lead, copper, mercury, cobalt, nickel, iron [ferrous or ferric], calcium, and barium).

β . By dissolving potassium ferricyanide (80 grams) in water, and mixing therewith a solution of ferrous sulphate free from ferric salt, and containing about 3 grams of iron. The resulting blue precipitate is washed first by decantation with water free from air and containing potassium chloride, afterwards on a filter with pure water. The product thus obtained has the same composition as the preceding.

If the soluble blue prepared by either of these methods be treated with ferrous sulphate, Turnbull's blue, $Fe^2(CN)^{12}$, or $3Fe^2 \cdot (Fe^2)^4(CN)^{12}$, is produced; and if the ferrous be replaced by ferric sulphate, ordinary Prussian blue, $Fe^3(CN)^{12}$ or $2(Fe^2)^4 \cdot 3Fe(CN)^6$, is formed. This last fact explains the occurrence in commerce of Prussian blues consisting partly of Turnbull's, partly of ordinary Prussian blue, the reaction between potassium ferrocyanide, ferrous sulphate, and oxygen, giving rise to the salt with higher or lower percentage of iron, accordingly as the oxygen is in excess or not. Skraup's experiments have shown that, on the one hand, ferrous salts exert a reducing action on potassium ferricyanide, and that, on the other hand, ferric salts exert an oxidising action on the ferrocyanide. Moreover, neutral ferric hydroxide is reduced by potassium ferrocyanide to ferrosiferic oxide, and neutral ferrous hydroxide is oxidised by potassium ferricyanide to ferric hydroxide. There is therefore no ground for assuming that the iron-atoms in Turnbull's and in Prussian blue are in different states, especially since, as shown by the experiments above detailed, Turnbull's blue may be formed both from ferrous and from ferric compounds (Skraup).

For Wyruboff's views of the constitution of the Prussian blues, see his paper above cited; also the abstracts of it in *Chem. Soc. J.* 1877, i. 189, and *Jahresb. f. Chem.* 1876, 312.

FERRICYANIDES, $R^3Fe^III(CN)^6$.

Potassium Ferricyanide is conveniently prepared by adding to a cold solution of the ferrocyanide as much hydrochloric acid as will take one atom of potassium from two molecules of the salt, and then a cold clear solution of bleaching powder till ferric chloride gives no reaction. Any excess of acid is neutralised with chalk, and the solution evaporated to crystallisation. The first crop of crystals is pure; the subsequent crops contain traces of lime which can be entirely removed by a single recrystallisation. The yield is very large (*F. Rhien, Dingl. pol. J.* ccvi. 151).

Reduction.—Potassium ferricyanide is reduced to ferrocyanide by the action of certain metals, viz. magnesium, arsenic, thallium, and palladium. On laying a strip of palladium (not hydrogenised) in a $\frac{1}{2}$ per cent. solution of the ferricyanide for ten minutes, a quantity of the salt is reduced, sufficient to give a distinct reaction of Prussian blue with ferric chloride. Platinum and gold immersed in a solution of the

ferrieyanide, in contact with an electronegative element, such as antimony or gas-carbon, likewise become covered with a blue film (Böttger, *Chem. Centr.* 1872, 708).

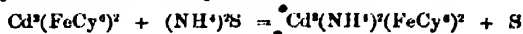
Potassium ferrieyanide is a powerful oxidiser, especially in presence of free alkali, but some of the other metallic ferrieyanides, especially the insoluble salts, such as those of zinc, copper, and mercury, act still more energetically, oxidising aniline salts to emeraldine or to aniline-black according to the concentration, &c.

A mixture of potassium ferrieyanide with ferric chloride gives at ordinary temperatures a brown precipitate with alcohol, cane-sugar, glucose, &c.; and if the same solution is applied to animal tissues, such as silk or wool, or placed in contact with oils, gums, starch, formic, uric, or arsenic acid, a green precipitate is formed having the properties of Pelouze's green cyanide. More energetic reducing agents—for example, hydrocyanic acid, tannin, aniline, wood, or skin—cause the formation of Prussian blue in a few seconds; methyl and amyl alcohols, benzene, gelatin, and cotton produce a similar action, which is not continuous, apparently indicating that only the impurities contained in these bodies are oxidised. Other substances, such as sulphides and sulphites, cause an immediate precipitate of Prussian blue. Insoluble sulphides act with but little less energy; and metals, such as iron, tin, copper, lead, and aluminium, act in a similar manner. When the solution is hot, these reactions take place more rapidly. Wool and silk may be thus dyed blue with great ease; the green tint at first produced is rapidly changed into blue by the action of a reducing agent. The blue colour may be combined with any other colour developed by oxidation, as catechu, indigo, &c. Wood, under the same circumstances, takes a splendid blue colour.

The purple colour produced by the action of a nitroprussiate on a sulphide becomes tolerably stable when immediately precipitated by zinc. A rose-coloured precipitate is thus obtained, which may be kept for a long time in the cold, but is decomposed on application of heat (Gaston Bong, *Bull. Soc. Chim.* [2], xxiv. 264).

Ferrieyanide of Lead and Potassium. $Pb^2K^2(FeCy)^2 + 3H_2O$, is formed, together with lead ferrieyanide, $Pb^2(FeCy)^2 + 16H_2O$, by mixing the hot solutions of equal parts of lead nitrate and potassium ferrieyanide, and leaving the liquid to cool. The lead ferrieyanide then separates out first, and the double salt is obtained by concentrating the mother-liquors. They are large, dark-red, six-sided plates belonging to the orthorhombic system. Axial ratio, $a : b : c = 1.7205 : 1 : 0.9309$. This salt is very soluble in water, and is precipitated by alcohol. Both the crystals and the aqueous solution decompose on exposure to the air (Wyruboff, *Ann. Chim. Phys.* [5], x. 409).

Ammonio-ferrocyanides of Cadmium. When ammonia in moderate quantity is poured upon cadmium ferrieyanide, the salt, $Cd^2(FeCy)^2 \cdot 2(NH^4)^2O$, is deposited in yellow scales, and, on adding excess of ammonia, red crystals are formed after some time, having the composition $Cd^2(FeCy)^2 \cdot 3(NH^4)^2O$. These crystals are monoclinic, having the axial ratio $a : b : c = 0.6160 : 1 : 1.2425$, and the angle $bc = 85^\circ 22'$. The red crystals, when exposed to the air for several days, give off ammonia, and are converted into a yellow crystalline powder identical with the yellow salt first described. At 110° this change takes place more quickly, and if the yellow powder thus obtained be heated with pure water or aqueous ammonia, a white powder is formed consisting of ammonioferrocyanide of cadmium and ammonium, $Cd^2(NH^4)^2(FeCy)^2 \cdot (NH^4)^2O$. The same salt is formed on drying the yellow scales for a few hours in contact with the air; also by the action of ammonium sulphide on cadmium ferrieyanide dissolved in aqueous ammonia:

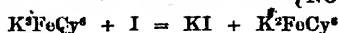


(Wyruboff, *ibid.* 413).

Bismuth Ferrieyanide. $Bi^2(FeCy)^3$ (bismuth quivalent), appears to be formed by precipitating a nearly neutral solution of bismuth nitrate with excess of a cold solution of potassium ferrieyanide. The yellow-green, slightly brownish precipitate thus obtained does not undergo any apparent change when washed with water by decantation in a closed vessel, but when it is dried at 100° hydrocyanic acid is given off, and the outer surface becomes covered with a greenish-blue film. An olive-green salt, likewise consisting of bismuth ferrieyanide,—somewhat contaminated however with Prussian blue resulting from a secondary decomposition—is obtained by warming the ferrocyanide with very dilute nitric acid (Muir, *Chem. Soc. J.* 1877, ii. 685).

New class of Prussiates, $R^2Fe^2Cy^4$. When iodine is added to potassium ferrieyanide, and the liquid heated nearly to the boiling point, a greenish-brown solution is formed, from which alcohol throws down a crystalline salt easily soluble in water. The solution of this salt, which is dark blue-green when concentrated

assumes on dilution a peculiar reddish or violet colour. The solution of the same salt in an alkali is decomposed by boiling, with separation of deep red ferric oxide. It has not been analysed, but the mode of its formation points to the formula above given, which is analogous to that of the nitroprussiates, $R^2Fe^{+}\left\{\begin{matrix} Cy^+ \\ NO \end{matrix}\right.$.



(Städeler, *Liebig's Annalen*, cli. 1).

According to Skraup (*Dent. Chem. Ges. Ber.* viii. 1503) and Bong (*Bull. Soc. Chim.* [2], xiv. 244) the same salt is obtained by treating potassium ferricyanide with potassium chlorate and hydrochloric acid. It is almost insoluble in alcohol, quite stable in air, and gives green precipitates with most metallic salts, even with zinc, whereby it is distinguished from the nitroprussiate, which gives a salmon-coloured precipitate with zinc (ii. 251). It is an energetic oxidiser, especially in presence of metallic salts. Nitric acid converts it into the nitroprussiate (Bong).

PLATINOCYANIDES, $R^2Pt(CN)^4$.

Fluorescence.—The platino-cyanides of the alkali-metals and alkaline earth-metals exhibit very varied fluorescence, each salt forming several hydrates, which differ from one another both in body-colour and in fluorescence. The body-colour is mainly determined by absorption of the fluorescent rays. Most of these salts exhibit very fine surface-colours (Hagenbach, *Pogg. Ann.* Jubelb. 1874, 303).

Thallious Platino-cyanide, $Tl^2Pt(CN)^4$. Friswell (*Chem. Soc. J.* 1871, 461) described a double salt of thallium cyanide and carbonate, $Tl^2Pt(CN)^4.Tl^2CO^3$, obtained by mixing the hot solutions of platino-cyanide of potassium or barium with thallious carbonate. This salt crystallises in rectangular prisms, crimson by transmitted, bronze-green with metallic lustre by reflected light. On treating it with warm nitric acid, the thallious carbonate is dissolved out, and on recrystallising the residue from water colourless crystals are obtained, consisting of thallious platino-cyanide, $Tl^2Pt(CN)^4$.

Carstanjen, in 1867, by mixing a neutralised and concentrated solution of hydrogen platino-cyanide with thallious carbonate, and evaporating, obtained blood-red needles with a splendid green metallic lustre in reflected light; these he regarded as thallious platino-cyanide (1st *Suppl.* 536). Friswell and Greenaway, however, find that when a solution of hydrogen platino-cyanide is mixed with an exactly equivalent quantity of thallious carbonate, a perfectly colourless salt is obtained having the composition of thallious platino-cyanide, $Tl^2Pt(CN)^4$, but that when twice that proportion of thallious carbonate is added, and the solution boiled, it deposits the dark red crystals of the double salt, $Tl^2Pt(CN)^4.Tl^2CO^3$. Thallious platino-cyanide is likewise obtained in colourless heavy crystals by decomposing barium platino-cyanide with thallious sulphate (*Chem. Soc. J.* 1877, ii. 251).

Haloid Derivatives of the Platino-cyanides. These compounds have been examined by Nils. Olof Holst (*Bull. Soc. Chim.* [2], xxii. 347, corresp.) with the following results:

Barium Bromoplatino-cyanide, $Pt(CN)^4Br^2Ba + 5H^2O$, produced by evaporating a solution of barium platino-cyanide mixed with bromine, forms yellow crystals permanent in the air, easily soluble in water and in alcohol. According to Topsoë, it crystallises in tetragonal prisms.

The **chloroplatino-cyanide**, $Pt(CN)^4Cl^2Ba$, and the **iodoplatino-cyanide**, $Pt(CN)^4I^2Ba$, closely resemble the bromine compound.

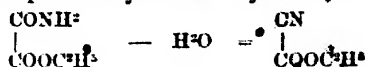
Hydrogen Bromoplatino-cyanide or **Bromoplatino-cyanhydric acid**, $Pt(CN)^4Br^2H^2 + xH^2O$, obtained by decomposing the barium salt with sulphuric acid, forms rather thick, tabular, deliquescent crystals, easily soluble in water and in alcohol. **Chloroplatino-cyanhydric acid** is obtained in a similar manner.

Potassium Bromoplatino-cyanide, $Pt(CN)^4Br^2K^2$, in the anhydrous state forms yellow tabular crystals, which are capable of taking up 2 mols. water and decompose at 200°. The corresponding **iodine compound**, $Pt(CN)^4I^2K^2$, forms tetragonal crystals permanent in the air. **Ammonium Bromoplatino-cyanide**, $Pt(CN)^4Br^2(NH^4)^2$, crystallises in yellow tabular or lenticular crystals of triclinic form.

The following salts have also been analysed:



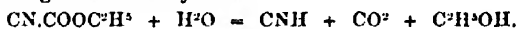
(Weddige, *J. pr. Chem.* [2], x. 193). *Ethyl Cyanocarbonate*, $\text{CN} \cdot \text{CO} \cdot \text{OC}^2\text{H}^5$, may be prepared, as already observed (2nd Suppl. 416) by the action of phosphoric anhydride on ethyl oxamate:



When equal weights of the two substances are heated together in a large retort, cyanocarbonic ether distils over at 120° , and the distillation may be continued up to 160° – 170° . The distillate may be purified by two rectifications.

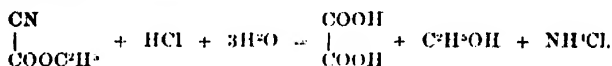
Ethyl cyanocarbonate is also formed, with evolution of hydrochloric acid, when ethyl dichloramidacetate (prepared by the action of PCl^3 on ethyl oxamate) is heated to its melting point: $\text{CCl}^2(\text{NH}^2) \cdot \text{CO} \cdot \text{OC}^2\text{H}^5 = \text{CN} \cdot \text{CO} \cdot \text{OC}^2\text{H}^5 + 2\text{HCl}$ (Wallach, *Deut. Chem. Ges. Ber.* viii. 299).

Cyanocarbonic ether purified as above, is a colourless, mobile, strongly refracting liquid boiling at 115° – 116° . It is lighter than water, mixes in all proportions with alcohol and ether, but is not miscible with water. When left for some time in contact with water, it decomposes into hydrocyanic acid, carbon dioxide, and alcohol, the decomposition being accelerated by heat:

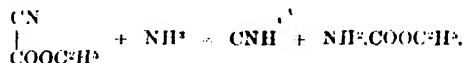


A similar reaction takes place with alkalis; the decomposition is not however complete, for the precipitate formed on adding silver nitrate to the resulting liquid does not consist of pure cyanide, but appears to contain also cyanocarbonate of silver. This salt has not however been isolated from it; neither has it been found possible to prepare any of the other metallic cyanocarbonates.

Concentrated hydrochloric acid resolves the ethylic ether into oxalic acid, ammoniac and alcohol:



Ammonia converts it into ethyl carbamate (urethane), a product also formed by the action of ammonia on chlorocarbonic ether:



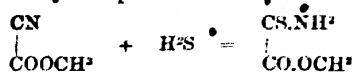
In like manner methylamine and aniline—the latter at 100° in sealed tubes—convert the ether into methyl- and phenyl-urethane.

Nascent hydrogen converts ethyl cyanocarbonate into the ethylic ether of amidacetic acid (ethyl-glycocine):



The reduction must be effected by hydriodic acid; for with sodium amalgam in alkaline solution the reaction above described with alkalis takes place; and with zinc and hydrochloric acid, it is for the most part the same as with hydrochloric acid alone (Weddige). According to Angelis, on the other hand (*Deut. Chem. Ges. Ber.* viii. 309), a mixture of ethyl cyanocarbonate and zinc, heated with hydrochloric acid, yields a large quantity of pure glycocine.

Methyl Cyanocarbonate, $\text{CN} \cdot \text{CO}^2\text{CH}^3$, is prepared by the action of phosphoric anhydride on methyl oxamate, and purified in the same manner as the ethylic ether, which it closely resembles. It is an ethereal, strongly refracting, pungent-smelling liquid, lighter than water, very soluble in alcohol and ether, insoluble in water. It boils without decomposition at 100° – 101° , and burns with a blue faintly luminous flame. By water it is decomposed more quickly than the preceding compound, and resolved into hydrocyanic acid, carbon dioxide, and methyl alcohol. Hydrogen sulphide converts it into methyl sulphoxamate:



Isobutyl Cyanocarbonate, $\text{CN} \cdot \text{CO}^2\text{CH}^2\text{CH}(\text{CH}^3)^2$, prepared like the preceding compounds, is a limpid liquid boiling at 146° , and having a pungent odour recalling that of isobutyl alcohol. It dissolves easily in alcohol and ether, but is insoluble in

618 CYANOCARBONIC COMPOUNDS, POLYMERIC.

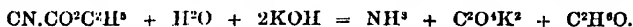
water, which decomposes it much more slowly than the ethylic or methylic ether. It burns with a bright flame (Weddige).

POLYMERIC CYANOCARBONIC COMPOUNDS.

Ethyl Paracyanocarbonate, $n\text{C}^2\text{H}^3\text{NO}^2$.—When ethyl cyanocarbonate is saturated with hydrochloric acid gas, and the liquid is heated to 100° for several hours in a sealed tube, or left to itself at the ordinary temperature for a few weeks, a crystalline product is obtained, having the same percentage composition as the original cyanocarbonic ether. The same crystalline product is obtained by the action of bromine under pressure, but a brominated product not very easily separated is formed at the same time, so that the former method is to be preferred.

Paracyanocarbonic ether crystallises in perfectly developed six-sided prisms which attain a considerable size, especially when formed by the gradual action of hydrochloric acid at ordinary temperatures. It is nearly insoluble in cold, and sparingly soluble in hot alcohol; still less easily in ether and in benzene, also in water whether hot or cold. It melts at 165° , but cannot be distilled or sublimed without decomposition; yielding, when heated above its melting point, a thick brown liquid, and emitting an odour like that of the alcoholic isocyanides; consequently its vapour-density cannot be determined. As it is solid at ordinary temperatures, whereas the cyanocarbonic ether previously described is liquid, it is inferred to be a polymeride of the latter, $n(\text{CN}.\text{CO}^2\text{C}^2\text{H}^3)$; but in the absence of a vapour-density determination, the value of n cannot be fixed.

Ethyl paracyanocarbonate, treated with caustic potash- or soda-solution at ordinary temperatures, yields paracyanocarbonate of potassium or sodium; but when boiled with the alkalis, it is resolved into ammonia and oxalic acid and ethyl alcohol:



It is likewise decomposed by concentrated acids, hydrochloric acid for example, with formation of oxalic acid.

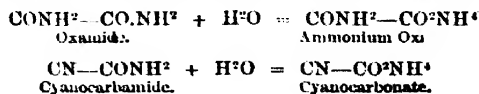
Paracyanocarbonic acid, $\text{C}^2\text{H}^3\text{NO}^2$.—The potassium salt of this acid is prepared by mixing the finely triturated ethylic ether with pure potash-ley, and leaving it till only a small quantity remains undissolved, and the liquid exhibits a neutral reaction. From the solution thus obtained, hydrochloric acid throws down the paracyanocarbonic acid, as a white bulky mass, mixed, however, with potassium chloride, from which it cannot be completely separated, as it is insoluble in alcohol and ether, not quite insoluble in cold water, and decomposed by boiling water.

The *potassium salt*, $\text{CN}.\text{CO}^2\text{K}$, is the only one of the paracyanocarbonates which crystallises well. It is obtained in long needles by slow evaporation in a vacuum, and is decomposed by boiling its solution with formation of potassium oxalate. The *silver salt*, $\text{CN}.\text{CO}^2\text{Ag}$, is obtained, on addition of silver nitrate to the potassium salt, as a yellow precipitate insoluble in nitric acid. The *calcium salt* is white, and dissolves in acetic acid, and in excess of water. *Acetate of lead* gives a white crystalline precipitate, *nitrate of silver* a yellow precipitate, soluble in ammonia, and reprecipitated by nitric acid. The *mercuric* and *mercurous* salts are white and yellow respectively; the *zinc* and *cadmium* salts white; the *iron* salt brown, and the *copper* salt green.

Methyl Paracyanocarbonate, $\text{CN}.\text{CO}^2\text{CH}^3$, may be prepared by heating methyl iodide and the silver salt with alcohol in sealed tubes to 100° ; also by the polymerising action of hydrochloric acid on methylic cyanocarbonate. It forms small needles melting at 134° .

Isobutyl Paracyanocarbonate melts at 158° .

Paracyanocarbamide, $\text{ON}.\text{CO}.\text{NH}^2$, formed by the action of warm aqueous, or, better, of alcoholic ammonia, on ethyl paracyanocarbonate, is a white amorphous substance nearly insoluble in water, alcohol, and ether. When heated it volatilises without previous fusion, giving off brown vapours with an odour of hydrocyanic acid. Acids and alkalis do not act upon it in the cold, but convert it into oxalic acid when heated. By prolonged boiling with aqueous ammonia, the amide is converted into ammonium cyanocarbonate, just as oxamide is converted into ammonium oxamate:



Paracyanocarbomethylamide, $\text{CN} \cdot \text{CONH}(\text{CH}_3)$, obtained like the preceding compound, with methylamine instead of ammonia, dissolves easily in hot alcohol and water, and crystallises on cooling in fine white needles having a silky lustre, which they lose when dried. It melts with decomposition at 250° , and behaves at a higher temperature like the amide, decomposing with emission of brown vapours, and emitting an odour like that of the nitrils.

Paracyanocarboxyphenylamide, $\text{CN} \cdot \text{CONH}(\text{C}_6\text{H}_5)$, produced by boiling together equivalent quantities of ethylic cyanocarbonate and aniline in alcoholic solution, is somewhat sparingly soluble in hot alcohol, from which it crystallises on cooling in slender lemon-yellow needles, resembling chloranil when dry; in cold alcohol and in water it is nearly insoluble. It cannot be sublimed without decomposition, and when heated above its melting point, it gives off brown vapours having an offensive odour. With acids and alkalis it behaves like the amide.

The cyanocarbonic ethers and their derivatives exhibit in all their reactions the closest analogy to the chlorocarbonic compounds (i. 916) (Weddige).

CYANOGEN. On the presence of Cyanogen in commercial bromine, see p. 350.

Cyanogen is quickly converted into paracyanogen by the action of the silent electric discharge (Berthelot, *Bull. Soc. Chim.* [2], xxvi. 101).

Cyanogen Chloride.—Weith (*Deut. Chem. Ges. Ber.* vii. 1745) observes that the preparation of this body, by passing chloring into a solution of mercuric cyanide, is often attended with very violent explosions. It is better prepared therefore from chlorine and hydrocyanic acid, the reaction then taking place without explosion.

On the structure of Polymeric Cyanogen-compounds, see Nencki (*Deut. Chem. Ges. Ber.* ix. 244; *Chem. Soc. J.* 1876, ii. 191).

CYANOMALONYL-URIC ACID, $\text{C}^6\text{H}^4\text{N}^2\text{O}^2$. An acid produced by the action of cyanogen gas on barbituric acid. See URIC ACID, DERIVATIVES OF.

CYANONAPHTHALENE, $\text{C}^{10}\text{H}^7\text{CN}$. α -Cyanonaphthalene, the nitril of α -naphthoic acid, is produced, together with naphthylamine, by heating sulphocarbonylnaphthalide with finely divided copper (Weith, *Deut. Chem. Ges. Ber.* vi. 967).

CYANOPHENYL ALCOHOL, $\text{C}^6\text{H}^4(\text{CN})\text{OH}$ (Griess, *Deut. Chem. Ges. Ber.* viii. 859-860). This compound, isomeric with phenyl-carbimide, $\text{N}(\text{CO})(\text{C}^6\text{H}_5)$, is readily formed by boiling diazocyanobenzene sulphate with a large quantity of water, and evaporating on a water-bath, after neutralising with ammonia. It crystallises from ether or alcohol in small white rhombic prisms, and from hot water in rhombic plates melting at 82° . It has an intensely sweet and pungent taste, and smells like phenol. On heating it with strong hydrochloric acid in sealed tubes in a water-bath, it is converted into oxybenzoic acid:



This alcohol, as well as the cyananiline from which it has been derived, belongs therefore to the meta-series.

Isocyanophenyl-chloride or **Phenyl isocyanochloride**, $\text{C}^6\text{H}_5\text{NCCl}_2$, produced by saturating a solution of phenyl thiocarbimide in chloroform with chlorine, has already been described (p. 602).

CYANURATE OF OXAMETHANE, $(\text{C}^6\text{O}^2\text{NH})^2 \cdot \text{C}^3\text{O}^2\text{N}^2\text{H}^2$ (Grimaux, *Bull. Soc. Chim.* [2], xxi. 153). This compound, polymeric with ethyl oxalurate, $(\text{C}^6\text{H}^4\text{N}^2\text{O}^4 \cdot \text{C}^2\text{H}^2)$, is formed when cyanic acid vapour is passed into fused oxamethane (m.p. 116° - 117°). It is best prepared by passing the vapour evolved by heating 3 grams of cyanuric acid into a vessel containing 5 grams of pure dry oxamethane heated in an oil-bath to 130° ; treating the product with 30 to 40 grams of boiling water; filtering; and purifying the needles which crystallise out (if they are still mixed with oxamethane) by recrystallisation.

Oxamethane cyanurate crystallises in shining brittle needles, nearly insoluble in cold water, soluble in about 30 pts. of boiling water. At 155° - 160° it melts to a pasty mass, and is resolved at a higher temperature into cyanic acid and a crystalline sublimate. On boiling it for a few minutes with milk of lime, and filtering, the filtrate deposits hard shining prisms of calcium oxamate. Ammonia added to the aqueous solution of oxamethane cyanurate throws down crystals of oxamide, and baryta-water produces a precipitate of barium cyanurate.

CYCLAMIN. This glucoside, obtained by De Luca from the tubers of *Cyclamen europeum* (ii. 204; 2nd Suppl. 418), has been further examined by L. Mutschler

(*Liebig's Annalen*, cxxxv. 214). It is extracted from the tubers with alcohol of 70 per cent., and after treatment with animal charcoal, forms a dazzling white powder, or white granules made up of microscopic needles. It is very hygroscopic, easily soluble in weak spirit, and more or less soluble in methyl and amyl alcohols, ethyl acetate, and glycerin; insoluble in ether, chloroform, carbon bisulphide, benzene, and petroleum spirit. Cyclamin is inodorous, but has an extremely acrid and bitter taste; its dust excites violent sneezing. It turns brown at 100°, and melts at 236°. The aqueous solution is opalescent, froths like soap-water, and produces a white precipitate in alkaline solution of cupric oxide, but does not reduce copper, even on long boiling. Strong sulphuric acid dissolves cyclamin with red colour; on diluting the solution with water, the colour disappears, and a white precipitate of cyclamiretin is thrown down, glucose remaining in solution. This decomposition of cyclamin into cyclamiretin and sugar is effected also by heating its aqueous solution to 95° for some time; by heating the dry substance to 100°; by prolonged exposure of the solution to direct sunshine; by the action of emulsin or beer-yeast; but most easily and completely by the action of dilute hydrochloric acid.

Cyclamin closely resembles saponin in physical and chemical characters, and is probably identical with it.

Cyclamiretin, $C^{15}H^{22}O^2$, is a white, amorphous, inodorous, and tasteless powder, dissolving in alcohol and ether, but not in water, melting at 198°. It is coloured violet by sulphuric acid. By fusion with potash it yields formic and butyric acids and other products. Nitric acid acting upon it produces resinous bodies, and ultimately oxalic acid.

Primulin, the substance extracted by alcohol from cowslip-roots (iv. 725), appears from Mutschler's experiments to be identical with cyclamin.

CYMENE, C^9H^{14} . The identity of the cymenes obtained from various sources has been demonstrated by the experiments of Wright and others, already described (2nd Suppl. 419; see further Beckett & Wright, *Chem. Soc. Jour.* 1876, i. 1). Wright has since established the identity of the cymenes from absinthol and citronellol (pp. 1, 620) with the rest, and Fittica (*Liebig's Annalen*, clxxii. 303) has examined those obtained from camphor, *Ptychotis* oil, and thymol.

Thymocymene was prepared by heating together 4 pts. of thymol and 1 pt. of phosphorus pentasulphide in fine powder in a flask with inverted condenser; much sulphuretted hydrogen was evolved, and thiocymene (b. p. 230°) was simultaneously formed; the hydrocarbon isolated from this by fractional distillation, treatment with soda-ley, and repeated distillation over sodium, boiled at 175° (mercury-column wholly in the vapour), and dissolved in strong sulphuric acid without evolving sulphurous acid: this serves as a good test of purity.

Ptychotis cymene was prepared by fractional distillation of the expressed oil of *Ptychotis Ajoûn*, the portion boiling at 170°–210°, being heated with sodium and treated with dilute sulphuric acid and potassium dichromate, or with dilute permanganate of potassium, until it would bear the test of sulphuric acid. The purified product boiled at 175°–176° (mercury-column wholly in the vapour).

Camphor cymene was prepared by acting on camphor with phosphoric anhydride, in quantity sufficient to form (theoretically) cymene and metaphosphoric acid; the yield is thus 60–80 per cent.; whereas Pott's method with pentasulphide of phosphorus gives only 25–30 per cent.; after purification as before, this specimen boiled at 175° (mercury-column wholly in the vapour): Beilstein & Kupffer found the same number.

These three hydrocarbons were oxidised by dropping into gently boiling red nitric acid (sp. gr. 1.5); in each case *nitrotoluic acid* melting at 189° was produced: hence all these are methyl-propyl-benzenes (1st Suppl. 302). By acting on them with bromine, in presence of iodine, a bromocymene was produced, boiling at 228°–229° in each case, and by oxidising this with dilute nitric acid, *bromonitrotoluic acid* melting at 204°–205° was formed. Strong colourless nitric acid converts these cymenes into *nitrocymenes* of two kinds, one (α) fluid and incapable of distilling unaltered (save in a vacuum); the other (β) crystalline, and melting after due purification at 125°; by oxidation the fluid variety yielded a nitrotoluic acid different from the above-mentioned body, melting at 189°; the barium salt of this acid was readily soluble in water, and crystallised therefrom in starlike needles; the acid itself was soluble in 450 parts of water, and was readily soluble in alcohol of 90 per cent., and sublimed without melting; the solid nitrocymene yielded on oxidation a third modification of nitrotoluic acid, subliming without previous melting, practically insoluble in hot and in cold water, and only slightly soluble in alcohol of 90 per cent.; it is not, however, yet decided whether this product is homogeneous, or a mixture of isomeric compounds.

The cymene-sulphonates of barium prepared from these three substances contained, in each case, $(C^{10}H^{14}.SO^2)Ba.3H^2O$.

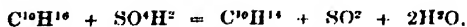
The same properties are exhibited by normal propyl-methyl-benzene prepared by the action of sodium on a mixture of bromotoluene, (m. p. 29°) and normal propyl bromide dissolved in pure anhydrous ether. This hydrocarbon boils at 175° – 176° ; gives paratoluic and terephthalic acids by oxidation with nitric acid and chromic acid respectively; and is converted by fuming nitric acid into a liquid and a solid nitro-cymene identical with the nitrocymenes obtained from the sources above mentioned, the solid modification melting at 125° , and the liquid yielding by oxidation a nitro-toluic acid identical with that obtained from the nitrocymenes above described.

Hence it may be inferred that Ptychotis oil, thymol, and camphor yield one and the same cymene, and that this hydrocarbon is identical with normal propyl-methyl-benzene and not with isopropyl-methyl-benzene, the contrary result obtained by other experimenters (1st Suppl. 302) being doubtless attributable to the imperfect purity of the materials used.

For the preparation of cymene from camphor, Paternò heats a mixture of 780 grams camphor, 100 red phosphorus and 265 flowers of sulphur, and boils the fused mass as long as hydrogen sulphide continues to be evolved. This is preferable to Pott's original method of heating camphor with ready-formed pentasulphide of phosphorus, as the action is much more regular.

Cymene from Turpentine oil.—Kekulé & Bruylants (*Deut. Chem. Ges. Ber.* vi. 437) have obtained cymene by the action of iodine on turpentine oil, the iodine being added by small portions, and the liquid each time heated till the reaction is ended, before another portion is added: these precautions are necessary on account of the violence of the action. The liquid is then heated for some time in a flask attached to a reversed condenser, afterwards repeatedly distilled, and the more fluid portions of the product is washed with potash-solution and rectified. By this process, 60 grams of turpentine oil and 23 of iodine yield about 10 grams of cymene. A hydrocarbon of higher boiling point, probably colophene, is also formed at the same time. The formation of the cymene takes place by addition of 1 mol. iodine to 1 mol. turpentine oil, forming the compound $C^{10}H^{14}I^2$, and the resolution of this compound by prolonged heating into $2HI$ and $C^{10}H^{14}$.

Riban (*Bull. Soc. Chim.* [2], xx. 100, 244) obtained cymene, together with terebene and other hydrocarbons, by the action of sulphuric acid on turpentine oil. Wright (*Chem. Soc. Jour.* 1873, 700) supposed that the cymene thus obtained was originally present in the turpentine oil, and was not produced by the oxidizing action of the sulphuric acid, inasmuch as by careful treatment of turpentine oil with sulphuric acid, he obtained only very small quantities of sulphurous acid, whereas by distilling the product with steam, and subsequent fractional distillation, he obtained about 3 per cent. of cymene. Riban, on the other hand, while admitting that crude oil of turpentine sometimes contains cymene, states that, in the experiments above referred to, he used perfectly pure turpentine oil boiling at 156° – 160° , and obtained from it, by treatment with the smallest possible quantity of sulphuric acid, about 7 to 8 per cent. of cymene. He also finds that, on treating turpentine oil with sulphuric acid at comparatively low temperatures, considerable quantities of sulphurous acid are given off and 7 to 8 per cent. of cymene is produced. He therefore maintains that cymene is formed from oil of turpentine by the action of sulphuric acid, even in the cold, according to the equation:



These results, obtained by Riban, are corroborated by Wright in a subsequent communication (*Chem. News*, xxix. 41).

The identity of the cymene from turpentine oil with that obtained from camphor, has been demonstrated by Paternò (*Gazz. chim. ital.* iv. 113) by a comparison of the cymene-sulphonic acids obtained therefrom.

Cymene is one of the constituents of Eucalyptus oil (Homeyer, *Arch. Pharm.* [3], v. 385).

The hydrocarbon called *cymene*, obtained by distilling worm-seed oil with phosphorus pentoxide (ii. 298) or pentasulphide (Graebe, *Uter.* v. 680), has been shown by Faust & Homeyer (*ibid.* vii. 1427) to be identical with cymene.

Reactions.—1. With Oxidising Agents.—Cymene (from terpene), heated for several hours with a mixture of 1 pt. nitric acid, sp. gr. 1.35, and 3 pts. water, yields a large quantity of terephthalic acid and a small quantity of paratoluic acid (m. p. 178°). Similar results are obtained with cymene from lemon oil (Oppenheim, *Ber.* vi. 915). Cymene from Ptychotis oil yields by oxidation with dilute nitric acid, chiefly toluic acid; with chromic acid mixture, terephthalic and acetic acids (Landolph, *ibid.* 937).

2. With *Iodine chloride*.—Cymene treated with iodine chloride, yields perchlorobenzene, perchloromethane, and perchloroethane (Krafft & Merz, *ibid.* viii. 1045).

3. With *Bromine*.—When cymene is heated with excess of bromine, in presence of aluminium bromide, toluene penta-bromide (m. p. 282°–283°), and isopropyl bromide (b. p. 60°–63°) are formed. The reaction, which takes place at 0°, is represented by the equation $C^{10}H^{14} + 5Br^2 = 4HBr + C^3H^7Br + C^3H_7Br^2$, and is a striking instance of the decomposition, at a comparatively low temperature, of an aromatic hydrocarbon, with formation of a body belonging to the methyl series. The products are obtained in quantities corresponding almost exactly with those required by the above equation.

The formation of isopropyl bromide in this reaction may be explained on two hypotheses: (1), that the cymene employed has the constitution of isopropyltoluene, and is resolved by the action of bromine into its constituent radicles; (2), that the bromide in question is formed by the addition of HBr to propylene, this body being produced according to the equation, $C^{10}H^{14} + 5Br^2 = C^3H^3Br^2 + 5HBr + C^3H^4$ (Gustavson, *Bull. Soc. Chim.* [2], xxvi. 346).

Bromocymene, $C^{10}H^{12}Br$. A solution of this compound in xylene, mixed with a little ethyl acetate, is readily attacked by sodium-amalgam, with production of mercuric cymilide, $Hg(C^{10}H^{12})_2$, which crystallises in matted needles, soluble in benzene and xylene, melting at 134°, and subliming without decomposition.

Bromocymene, heated to 100° with a mixture of strong nitric and fuming sulphuric acid, yields two crystalline sulphoacids which are difficult to separate (Paternò & Colombo, *Ber.* x. 1749).

Chlorocymenes, $C^{10}H^{11}Cl = C^6H^3Cl \begin{smallmatrix} CH^3 \\ C^3H^7 \end{smallmatrix}$ (E. & Gerichten, *Ber.* x. 1249; xi. 364). Chlorine in presence of iodine acts readily on cymene (from camphor), forming a nearly colourless chlorocymene, having a density of 1.014 at 14°, boiling at 208°–211°, and yielding by oxidation with dilute nitric acid (after five hours' boiling) a chlorotoluic acid, $C^6H^3Cl(CH^3)(CO^2H)$, which crystallises in large laminae melting at 196°. When, on the other hand, cymene obtained from thymol is boiled with dilute nitric acid for fourteen days, the liquid on cooling deposits crystals of an acid which, when purified by solution in potash, precipitation by hydrochloric acid, conversion into barium salt, and separation therefrom, crystallises from alcohol in long needles, the analysis of which agrees, not with the formula of chlorotoluic acid, $C^6H^3ClO^2$, but with the formula, $C^{10}H^{11}ClO^2$, which may be that of methylchlorhydrocinnamic

acid, $C^6H^3 \begin{smallmatrix} \diagup Cl \\ \diagdown CH^3CH^2COOH \end{smallmatrix}$, or that of a chlorinated isomeride of cumic

acid, $C^6H^3 \begin{smallmatrix} \diagup Cl \\ \diagdown COOH \end{smallmatrix}$

v. Gerichten represents the constitution of the two chlorocymenes, and of the acids which they yield on oxidation by the following formulae:

Chlorocymene from cymene ($C^6H^3 : Cl : CH^3 = 1 : 3 : 4$) gives by oxidation chlorotoluic acid, $COOH : Cl : CH^3 = 1 : 3 : 4$.

Chlorocymene from thymol ($C^6H^7 : Cl : CH^3 = 1 : 2 : 4$) gives an isomeride of chlorocumic acid ($COOH : Cl : C^3H^7 = 1 : 2 : 4$), or else methyl-chlorhydrocinnamic acid ($CH^3.CH^2.COOH : Cl : CH^3 = 1 : 3 : 4$).

Nitrocymenes (Landolph, *Ber.* yi. 936). Two mononitrocymenes, $C^{10}H^{11}NO^2$ (α and β), are obtained from camphor cymene. The nitration is best effected with nitric acid of sp. gr. 1.4, at a temperature of 40°–50°; and on washing the product with aqueous sodium carbonate and water, and distilling it with steam, α -nitrocymene passes over as a light yellow liquid having a faint odour of cymene, a density of 1.0385 at 18°, and not volatile without decomposition. From the small quantity of resinous residue of the distillation, β -nitrocymene may be obtained by crystallisation from alcohol in needles melting at 124.5°.

α . Nitrocymene, oxidised with chromic acid mixture, yields a nitrotoluic acid which is very slightly soluble in cold water, somewhat more easily in hot water; crystallises from dilute alcohol in small needles or laminae; sublimes without previous fusion; and forms a barium salt which dissolves readily in water, and crystallises from the concentrated solution in stellate groups of slender needles (compare v. 862).

Dinitrocymene, $C^{10}H^9(NO^2)_2$, is obtained by the action of nitric acid, sp. gr. 1.5, on cymene (from Ptychotis oil) in the form of a liquid which may be purified by

distillation with steam. Sp. gr. = 1.206 at 18°; 1.204 at 21°. Together with this dinitrocymene there is also formed a small quantity of a body melting at 178°–180° (trinitrocymene?) and a nitrotoluic acid different from that which is produced from α -nitrocymene. This nitro-acid melts at 183.5°–184.5°, dissolves sparingly in cold, more freely in hot water, and crystallises therefrom in tufts of long needles. From alcohol, in which it is easily soluble, it crystallises in small needles.

Another dinitrocymene, solid at ordinary temperatures, is obtained by leaving coal-tar cymene for several days in contact with fuming nitric acid. It is nearly insoluble in cold alcohol, and only slightly soluble in hot alcohol, from which it separates in small colourless crystals melting at 205° (A. Rommier, *Bull. Soc. Chim.* [2], xix. 434).

CAM or THIOCYMENE, $C^{10}H^{12}SH$ (Fittica, *Liebig's Annalen*, clxxii. 324. Bechler, *J. pr. Chem.* [2], viii. 167). Fittica prepares thymothiocymene by heating thymol with a quantity of phosphorus trisulphide sufficient for the formation of phosphorous acid. From the product of this reaction, pure thiocymene is easily obtained by fractional distillation, as scarcely any cymene is formed at the same time. The same compound is formed in small quantity in the preparation of cymene from thymol by the action of phosphorus pentasulphide, and may be separated by agitating the portion of the distillate boiling between 210° and 240° with mercuric oxide, boiling with alcohol, and decomposing the mercury-compound, which remains after evaporation of the alcohol, with hydrogen sulphide.

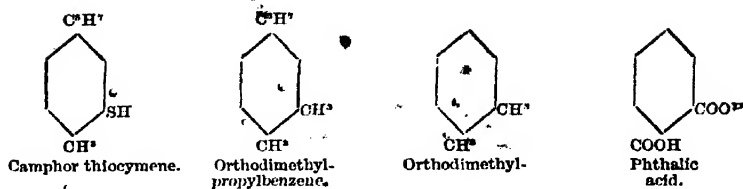
Thymothiocymene is a nearly colourless liquid which boils at 230°–231°, does not solidify at –20°, and has a peculiar pungent odour, not at all like that of the mercaptans of the fatty group. Sp. gr. = 0.989. Its mercury salt, $(C^{10}H^{12}S)^2Hg$, forms greenish rhombohedral crystals melting at 78°, rather sparingly soluble in alcohol. The lead salt, $(C^{10}H^{12}S)^2Pb$, obtained by precipitating the alcoholic solution of the thiocymene with lead acetate, crystallises from alcohol in golden-yellow needles. On dropping an alcoholic solution of thymothiocymene into alcoholic silver nitrate, a yellowish precipitate is formed which soon becomes dirty-white and remains amorphous.

Thymothiocymene, oxidised with nitric acid, yields a sulphotoluic acid different from that which Flesch obtained by similar treatment of camphor-cymene (*2nd Suppl.* 421). This result, together with the characters of the mercury and silver salts, and the boiling point of the mercaptan, shows that the thiocymenes from thymol and from camphor are not identical but isomeric.

The thiocymene from camphor has been further examined by Bechler, who prepares it by treating the potassium salt of the corresponding cymene-sulphonic acid with phosphorus pentachloride, and reducing the cymene sulphochloride thereby obtained with zinc and dilute sulphuric acid. It is a colourless, strongly refracting liquid, having a disagreeable sweetish odour, a sp. gr. of 0.995, and boiling at 233°. It volatilises with vapour of water, is insoluble in water, but easily soluble in alcohol and ether. The mercury-compound, $(C^{10}H^{12}S)^2Hg$, crystallises from alcohol in needles having a silky lustre. The lead-compound is yellow, uncrystallisable, insoluble in water, nearly insoluble in alcohol, but very easily soluble in ether, from which it always separates as an oil, which solidifies to a mass resembling colophony.

Camphor thiocymene does not yield any definite products with potassium permanganate or with bromine. The reaction with permanganate is energetic, and attended with considerable evolution of heat.

The methyl ether of camphor thiocymene, $C^{10}H^{12}.SCH^3$, is obtained by adding the calculated quantity of sodium to an ethereal solution of thiocymene, and mixing the product with an equivalent quantity of methyl iodide, keeping the mixture cool in both stages of the reaction. It is a strongly refracting, rather disagreeably smelling liquid, having a specific gravity of 0.986, and boiling at 244°. On passing the vapour of this ether over heated copper turnings, and treating the resulting hydrocarbon with nitric acid, an acid $C^8H^8(CH^3)^2.CO^2H$ is formed, which dissolves in water, alcohol, and ether, and sublimes in fine white needles. The hydrocarbon (dimethyl-benzene) obtained by distilling this acid with quicklime, yields, on oxidation with chromic acid mixture, acetic but no isophthalic acid; needle-shaped crystals were, however, found in the condensing tube, which appeared to consist of phthalic anhydride. Supposing this to be the case, the results above described may be explained by assigning to camphor thiocymene the constitution represented on p. 624, the SH group being adjacent to the methyl group. On treating this compound as above described, the hydrogen in the SH group is first replaced by sodium, and this again by methyl. The sulphur is then removed, leaving orthodimethyl-propyl-benzene (the two methyl groups contiguous); this hydrocarbon, treated with nitric acid, yields the acid $C^8H^8(CH^3)^2.CO^2H$, the propyl group being replaced by CO^2H , and this acid, distilled with lime, yields orthodimethyl-benzene, convertible by oxidation into phthalic acid: thus—



The thiocymene from thymol will be represented by a similar formula, in which the SH group is contiguous to the propyl group, and the corresponding oxycymenes will have the formula represented below:



CYMENE-SULPHONIC ACID, $C^{10}H^{14}.SO^3H$. When β -nitrocymene is gently heated with strong sulphuric acid, the product poured into water, and the mixture left to cool, a cymene-sulphonic acid separates out, different from that previously described (1st Suppl. 420). It is nearly insoluble in cold water, and crystallises from hot water in thick microscopic prisms melting at 177° (Fittica, *Deut. Chem. Ges. Ber.* vii. 1360).

Cymenesulphamide, $C^{10}H^{14}.SO^2.NH^2$, produced by the action of alcoholic ammonia at 120° – 140° on cymenesulphochloride, forms small white laminae, which, when purified by recrystallisation from boiling water with the aid of animal charcoal, melt at 143° . On mixing its solution in boiling water with 1 mol. silver acetate, likewise dissolved in hot water, a white precipitate is formed, consisting of silver cymenesulphamide, $C^{10}H^{14}.SO^2.NHAg$.

Cymenesulphinic acid, $C^{10}H^{14}.SO^3H$.—The zinc salt of this acid is formed by the action of zinc-dust and water on cymenesulphonic chloride, and the acid itself is obtained by decomposing this salt with sodium carbonate, and the resulting sodium salt with hydrochloric acid. On agitating the liquid with ether, and leaving the ethereal solution to evaporate, the cymenesulphonic acid remains as a yellow syrup but slightly soluble in water. The silver, copper, and lead salts are obtained as precipitates; the potassium salt by neutralisation and evaporation in colourless crystals, which, when pressed and air-dried, have the composition $C^{10}H^{14}.SO^2K + 3\frac{1}{2}H^2O$. The silver salt, treated with the iodides of ethyl and propyl, gave syrupy ethers which were decomposed by distillation (Bergor, *Ber.* x. 976).

CYMYL-PHENYL KETONE, $C^{10}H^{12}.CO.C^6H^5$. See KETONES, AROMATIC.

CYNANCHOL. This name was given by Butlerow (*Liebig's Annalen*, cxxx. 349) to a substance crystallising in needles and in plates, which he obtained from the sap of *Cynanchum acutum*, a creeping plant of the Apocynaceae order, growing in the neighbourhood of the river Oxus, where it is regarded as very poisonous, and especially dangerous to camels. Butlerow did not, however, succeed in extracting any poisonous principle from it. According to Hesse (*ibid.* cxxxii. 163), the so-called cynanchol is a mixture of echicerin and echitin (substances existing in Dita bark, q.v.), the former crystallising in needles, the latter in plates. To effect their separation it is necessary to operate on large quantities of material.

CYPRESSUS. From the leaves of *Cypressus pyramidalis*, Hartsen (*Compt. rend.* lxxiii. 1614) obtained an amorphous yellow substance soluble in alcohol, and precipitated by an alcoholic solution of neutral lead acetate. The fruits of the same plant yielded a substance crystallising in prisms, soluble in alcohol and likewise precipitated by acetate of lead.

CYSTINE (ii. 300). The behaviour of this substance with various reagents has been studied by Dewar & Gamgee (*Pharm. J. Trans.* 1870, p. 385). On adding am-

moniacal silver nitrate to a solution of cystine in strong aqueous ammonia, no alteration takes place at ordinary temperatures, but on adding nitric acid, a canary-yellow precipitate is formed, apparently consisting of a compound of cystine with silver nitrate; the filtrate blackens when heated. The ammoniacal solution of cystine, mixed only with silver nitrate, deposits silver sulphide when heated, without formation of sulphuric or oxalic acid. On heating cystine with caustic soda, sodium sulphide is formed; with baryta-water at 150° , the products are barium sulphide and sulphite, with traces of thiosulphate. On heating it to 130° with alcoholic potash, distilling off the alcohol, and exhausting the acidulated residue with ether, there is obtained, after evaporation, a non-crystallising substance free from sulphur and having a strong acid reaction. Cystine treated with zinc and sulphuric acid gives a considerable quantity of hydrogen sulphide (taurine similarly treated gives none). Cystine heated under water with nitrous acid dissolves, forming a clear liquid, which contains sulphuric but no oxalic acid, and reduces silver nitrate.

J. H. Müller (*Zeitschr. Anal. Chem.* 1873, 234) has examined urinary calculi of the size of peas consisting of pure cystine. For the recognition of this substance, he recommends dissolving it in potash-ley, and testing the solution for potassium sulphide with a nitroprusside.

L. Gmelin assigned to cystine the formula $C^6H^8NSO^2$. It appears, however, from the experiments of Dewar (*Pharm. J. Trans.* [3], vii. 144), that cystine treated with nitrous acid yields a product agreeing in its characters with the syrupy modification of pyruvic acid, $C^3H^4O^3$. Hence it is probable that cystine has the constitution of amido-thiopyruvic acid, $C^6H^8NO^3S$, and contains only 6 atoms of hydrogen. Dewar finds moreover, that cystine treated with sodium-amalgam does not yield alanine, $C^3H^7NO^2$; hence it appears that the sulphur is not replaceable by hydrogen. The relation of cystine to pyruvic acid may therefore probably be represented as follows:



The quantities of cystine, urea, and uric acid contained in the urine excreted in 24 hours, on 14 consecutive days, by a patient suffering from cystinuria, have been determined by W. F. Löbisch (*Liebigs Annalen*, lxxxii. 231). The mean numbers found were for urea 33.28 grams, for uric acid 0.5545, for cystine 0.393, the quantities of urea and uric acid exhibiting no deviation from the normal amounts. Löbisch is of opinion that the alleged decrease in the excretion of these substances in previously described cases of cystinuria must have been due to changes in the organism accompanying the cystinuria, but not necessarily connected with it.

D

DAMMARA RESIN. *Kauri or Cowdrie Gum.*—This gum-resin, the produce of *Dammara australis*, a large tree growing in New Zealand, was examined in 1843 by R. C. Thomson (ii. 301), and has been further examined by M. M. P. Muir (*Chem. Soc. J.* 1874, p. 733), who finds that it has a specific gravity of 1.042, and is partly soluble in water, partly in alcohol, and partly in ether. The alcoholic solution contains traces of benzoic and succinic acids. It is very strongly attacked by chlorine, bromine, and concentrated nitric acid, and dissolves at ordinary temperatures in strong sulphuric acid, forming a red liquid from which water throws down a white substance. In solutions of caustic alkalis it swells up and partly dissolves. By dry distillation it yields a volatile oil which boils between 155° and 156° , and gives by analysis 79.07 per cent. carbon and 10.90 hydrogen, indicating the formula $C^{10}H^{20}O^1$ (Thomson found 82.2 carbon and 11.1 hydrogen).

DAMOURITE. On Damourite accompanying Corundum, see Genth (*J. pr. Chem.* [2], ix. 49; *Jahresb. f. Chem.* 1873, 1151).

DATES. The kernels of dates have been analysed by F. H. Storer (*Bulletin of the Bussey Institute*, i. 373), with the following results:

3rd Sup.

S S

Water	Ash	Proteids	Carbohydrates and Fat	Cellulose
9.27	1.04	5.46 C	61.17	23.06 = 100.

The dry organic matter amounts to 89.70 per cent., the fat to 8.50, and nitrogen to 0.86. These results show that dates form a valuable article of food.

DATOLITE. This mineral occurs, associated with garnet and vesuvian, in a limestone at Santa Clara, California. It is colourless and crystalline, but does not exhibit distinct faces, sp. gr. = 2.988. Analysis gave—

SiO ²	B ² O ³	CaO	H ² O
38.02	21.62	33.87	5.61 = 99.12

(J. L. Smith, *Sill. Am. J.* [3], viii. 434).

The monoclinic character of datolite, first demonstrated by E. Dana, has been confirmed by an examination of the optic and thermic characters by C. Bodewig (*Pogg. Ann.* clviii. 230; *Chem. Soc. J.* 1877, ii. 170).

DATURA. On the chemico-legal detection of *Datura Stramonium*, *Atropa Belladonna*, and *Hyoscyamus niger*, see Wasilewsky (*Chem. Centr.* 1877, p. 9; *Chem. Soc. J.* 1877, ii. 934).

DAUBREILITE. This name is given by J. L. Smith to a sulphide of chromium (62.38 per cent. Cr and 37.62 S), occurring as a coating and in veins of certain concretions found in masses of meteoric iron from the Mexican Desert (*Sill. Am. J.* [3], xii. 107; *Jahrb. f. Chem.*, 1876, 1314).

DAUBREITE. An oxychloride of bismuth from the bismuth mine of Constanca in Bolivia, where it occurs somewhat abundantly, as a yellowish or greyish earthy mass containing a large quantity of opaque crystalline nacreous plates, which sometimes give it almost a fibrous texture. Hardness = 2 to 2.5. Sp. gr. = 6.4 to 6.5. Analysis shows it to contain 72.60 per cent. Bi²O³, 22.62 BiCl³, 3.84 H²O, and 0.72 Fe²O³, a composition which, neglecting the water and ferric oxide as unessential, leads to the formula BiCl³.4Bi²O³, intermediate between those of the two known artificially prepared oxychlorides, BiCl³.2Bi²O³ and BiCl³.6Bi²O³ (Domeyko, *Compt. rend.* lxxiii. 922).

DAVYUM. A metal recently discovered in Russian platinum ore by S. Kern (*Compt. rend.* lxxv. 72; *Chem. News*, xxxvi. 114; *Chem. Centr.* 1877, pp. 562, 692). The ore, containing 80.03 per cent. platinum, 9.15 iridium, 0.61 rhodium, 1.35 osmium, 1.20 palladium, 0.45 iron, 0.28 ruthenium, 1.02 copper, was treated by Bunsen's method (*Phil. Mag.* [4], xxxvi. 253; *Jahrb. f. Chem.* 1868, 280), to separate the metals, and the mother-liquor which remained after separating the rhodium and iridium was heated with excess of chloride and nitrate of ammonium. The dark red precipitate thereby formed gave on ignition a grey metallic mass resembling platinum sponge, and this, when fused before the oxy-hydrogen blowpipe, yielded the new metal in the form of a metallic button having a silver-white colour (0.27 gram from 600 grams of the ore, or about 0.045 per cent.)

The atomic weight of davyum is nearly 154. Sp. gr. 9.389. The metal is hard, but malleable when heated; it is easily attacked by aqua regia; very slightly by boiling sulphuric acid. A solution of the chloride gives with *potash* a light lemon-yellow precipitate easily soluble in acids, even in strong acetic acid. *Hydrogen sulphide* forms a brown precipitate becoming black when dry. *Potassium thiocyanate* colours the solution deep red, and in a concentrated solution forms a red precipitate, which, when dried over sulphuric acid, yields red crystals of davyum thiocyanate, changing when heated in a sand-bath into a black mass having the same composition as the crystals. An acid solution of the chloride gives with *potassium ferrocyanide* a brown precipitate.

Davyum chloride forms crystals easily soluble in water, alcohol, and ether, and absorbing but little moisture from the air. When heated before the blowpipe it is converted into the monoxide, which is insoluble in all acids except aqua regia. Davyum chloride unites with the *chlorides of potassium, ammonium and thallium*, yielding double chlorides in the form of dark red crystals slightly soluble in water, insoluble or nearly so in alcohol. The *sodium salt* is nearly insoluble in water as well as in alcohol, a character which distinguishes davyum from all the other platinum-metals, the sodium double chlorides of which are easily soluble in water.

Davyum chloride dissolves easily in *potassium cyanide*, the solution yielding on evaporation prisms of potassium-davyum cyanide, the potassium in which may be replaced by various other metals, forming soluble double cyanides.

Davyum sulphate, obtained by heating the metal with sulphuric acid, is a yellowish-red powder nearly insoluble in water. The sulphide, obtained by passing

through the acid solution of a davyum salt, is a brown precipitate; turns black when dry, and dissolves in the sulphide of the alkali-metals, probably forming sulphur-salts.

On the spectrum of davyum volatilised in the electric arc, see *Compt. rend.* lxxxv. 667; *Chem. Centr.* 1877, 754.

DAWSONITE. This mineral occurs in the clefts of a trachytic rock situated to the west of McGill College, in Canada. It has a fibrous texture. Hardness = 3. Sp. gr. = 2.40. White. Transparent. Before the blowpipe it turns deep yellow and swells up. Dissolves with effervescence in hydrochloric acid. Two analyses gave—

CO ²	Al ² O ³	CaO	MgO	Na ² O	P ₂ O ₅	H ² O	SiO ²	
29.88	32.84	5.95	trace	20.20	0.38	11.91	0.40	= 101.56
30.72	32.68	5.65	0.46	20.17	—	10.32	—	= 99.99

(Harrington, *Canadian Naturalist*, vii. 6).

DECARBOMODIPHENYLAMINE. See PHENYLAMINES.

See NAPHTHALENES.

D, C⁶H⁵O⁴. This acid dissolved in phosphorus oxychloride reacts with the pentachloride in such a manner as to form *dehydracetic chloride*, C⁶H⁵O²Cl³, that is dehydracetic acid in which two hydroxyl-groups are replaced by chlorine. This substance crystallises in reddish needles which melt at 101°. It is decomposed by distillation *per se*, but volatilises with water-vapour. When heated to 200° with water, it is converted into dehydracetic acid.

Dehydracetamide, C⁶H⁵O⁴.NH², is obtained by evaporating a solution of dehydracetic acid in aqueous ammonia, or by evaporating a solution of the ethyl ether of the acid in alcoholic ammonia. It is a crystalline substance melting at 208.3°, and dissolving easily in alcohol, ether, and hot water. It sublimes without decomposition.

Dehydracetanilide, C⁶H⁵O⁴.NHC⁶H⁵, is formed by warming the acid with excess of aniline. It crystallises in white needles, which dissolve in alcohol and ether, melt at 115°, volatilise with aqueous vapour, and decompose when heated. It dissolves in dilute hydrochloric acid, and forms a very unstable double salt with platinum chloride.

Monochlorodehydracetic acid, C⁶H⁵ClO⁴, obtained by passing chlorine into a solution of the acid in chloroform, crystallises in needles which melt at 93°.

Monobromodehydracetic acid, C⁶H⁵BrO⁴, is formed on heating a solution of the acid in chloroform to 30°–40° with bromine. It is a yellowish crystalline body melting at 134° (Oppenheim u. Procht, *Deut. Chem. Ber.* ix. 1099).

See ACETONAMINES (p. 31).

This resin, which exudes from *Gardenia lucida*, an East Indian plant, has a well-marked odour, is yellow when powdered, and dissolves with yellow colour in alcohol (0.82 sp. gr.), the solution having a fine yellow colour, with a well-marked greenish tinge. It is neutral to litmus paper, but is coloured deep greenish-brown by ferric chloride. Fused with caustic potash it yields a substance which on treatment with acid forms an addition compound.

portion of "dekamali" is also soluble in alcohol, and yields with lead acetate a yellow precipitate, lead also remaining combined in solution. The precipitate yielded on decomposition a small quantity of resin, and the solution appeared to contain a resin melting below 100°, and yielding by analysis numbers approximately represented by the formula, C²²H³⁴O⁴ (Flückiger, *Pharm. J. Trans.* [3], vii. 589).

DELPHINE. On the separation and estimation of this alkaloid, see PLANT-ALKALIDS.

DELVAUXITE. This mineral occurs in nodules with botryoidal surfaces on veins at the outcrop of brown hematite. Its colour is brown, liver-brown, chestnut-brown to black; fracture conchoidal; lustre pitchy. It is brittle, and falls to pieces after a while, in consequence of gradual desiccation. When air-dry it still contains a considerable quantity of hygroscopic water, which it loses after some time over calcium chloride, but recovers on exposure to the air. After gentle ignition, whereby it loses all its water, it forms a brown-red powder, and melts before the blowpipe to a grey magnetic bead. The specific gravity of the air-dried mineral varies between

• With trace of ferric oxide.

1.85 and 2.25, increasing as the quantity of hygroscopic water diminishes. When completely freed from hygroscopic water by drying over calcium chloride, it has a sp. gr. of 2.697–2.707. It dissolves very easily in cold strong hydrochloric acid, with separation of flocks of silica, forming a brown solution. In warm acids, even when very dilute, it dissolves with unusual facility. In water many varieties decrepitate but without disintegrating; others do not decrepitate at all.

The chemical composition of the mineral dried over calcium chloride answers most nearly to the formula, $2\text{CaO} \cdot \text{P}_2\text{O}_5 + 5\text{Fe}^2\text{O}_3 \cdot \text{P}_2\text{O}_5 + 16\text{H}_2\text{O}$; it may also be nearly represented by $\text{CaO} \cdot 2\text{Fe}^2\text{O}_3 \cdot \text{P}_2\text{O}_5 + 7\text{H}_2\text{O}$ (Vála a. Helmhaecker, *Jahrb. f. Min.* 1875, 317).

DESCLOIZITE. See VANADATES.

DEWALQUITE. See ARDENNITE (p. 119).

DEOXYBENZOLIN, $\text{C}^{11}\text{H}^{10}\text{O} = \text{C}^6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}^6\text{H}_5$ (2nd Suppl. 176). This compound, heated to 150° in a sealed tube with alcoholic potash, yields stilbene hydrate and the potassium salt of diethylcarbobenzoic acid, $\text{C}^{10}\text{H}^{10}\text{O}_2$. This acid crystallises in white needles, soluble in alcohol and ether, and yields a white soluble sodium salt, and a white, amorphous, sparingly soluble silver salt. By the action of an ethereal solution of ethyl iodide, the dry silver salt is converted into ethylic diethylcarbobenzoate, which is a heavy oily liquid. Nitric acid dissolves diethylcarbobenzoic acid with a transient red coloration, and on addition of water dinitrodiethylcarbobenzoic acid, $\text{C}^{10}\text{H}^{10}(\text{NO}_2)_2\text{O}_2$, separates out as a white flocculent precipitate. On crystallisation from hot alcohol it yields white needles melting at 155° – 166° , and soluble in 26 pts. of boiling alcohol. By fusion with excess of alkali, potassium diethylcarbobenzoate is split up into potassium diethylbenzoate and potassium benzoate.

By heating to 150° in a sealed tube a mixture of deoxybenzoin and a solution of potassium hydroxide in normal propyl alcohol, there is formed stilbene hydrate and the potassium salt of dipropylcarbobenzoic acid, $\text{C}^{20}\text{H}^{22}\text{O}_2$. This acid crystallises partly in long thin plates and partly in heavy octohedrons. The octohedral crystals melt at 90° , and are easily soluble in alcohol and ether, whilst the thin plates are less soluble in these liquids, and melt at 139° . The latter yield with nitric acid rhombic plates, melting at 176° , soluble in 40 pts. of boiling alcohol, and having the composition of dinitrodipropylcarbobenzoic acid, $\text{C}^{20}\text{H}^{22}(\text{NO}_2)_2\text{O}_2$. The octohedral crystals yield by nitration a resinous body easily soluble in alcohol. Pseudopropyl alcohol does not act on deoxybenzoin in the same manner as the normal alcohol.

Deoxybenzoin heated to 140° – 142° with a solution of potash in isobutyl alcohol, yields the potassium salt of di-isobutylcarbobenzoic acid, $\text{C}^{22}\text{H}^{24}\text{O}_2$, which acid crystallises in rhombic plates melting at 148° , and soluble in 20 pts. of boiling alcohol; and with amyl alcohol in like manner, diamylcarbobenzoic acid, $\text{C}^{24}\text{H}^{26}\text{O}_2$, is obtained in long thin needles melting at 160° and dissolving in 28.5 pts. alcohol (Zagoumenny, *Deut. Chem. Ges. Ber.* viii. 265; *Lieb. Ann.* clxxiv. 163).

DEOXYGLUTAWIC ACID, syn. with NORMAL PYROTARTARIC ACID (q.v.)

DEOXYMESITYL OXIDE. See MESITYL OXIDE.

DEOXYPHORONE. See PHORONE.

DEXTRIN, $\text{C}^6\text{H}^{10}\text{O}_5$. *Manufacture*.—Anthon (*Dingl. pol. J.* ccxviii. 182; ccix. 457) prepares dextrin from the entire substance of potatoes in the following manner. The bruised potatoes are exhausted with acid or alkaline water, then washed and dried, and the dry substance, after being finely pulverised, is moistened with 5 to 10 per cent. of its weight of silicofluoric or borofluoric acid, then spread in the drying rooms on linen cloths, and heated, first at 33° – 34° , then at 70° – 75° , till its weight becomes constant, and finally for half-an-hour at 90° . The starch thus thoroughly dried is placed in tin-plate dishes, and heated in a salt-bath to 100° – 120° , till a sample taken out, cooled, and moistened with cold water, forms transparent vitreous globules. Good results were obtained with 10 pts. by weight of potato-starch dried at 40° – 50° , and 6.5 pts. of silicofluoric acid (1 pt. of acid at 6° Bm. to 7 water), the mixture being heated to 108° for nine hours.

Purification and Properties.—According to C. O'Sullivan (*Chem. Soc. J.* 1872, 580), dextrin, whether prepared by the action of acids, or of malt-extract (diastase) on starch paste, always contains sugar, which cannot be separated from it by mere precipitation with alcohol, but only by fermentation with yeast followed by repeated precipitation with alcohol. In this way a product may be obtained, which, when boiled for twenty minutes with Fehling's copper solution, exerts a reducing power equivalent to only 2 per cent. of glucose.

The purified dextrin thus obtained is a white brittle powder, sometimes containing shining particles, which, when examined by the microscope, exhibit no traces of crystallisation, but appear as fracture-surfaces. When dried over sulphuric acid it retains a molecule of water ($C^6H^{10}O_5 \cdot H^2O$), which is given off at 100° . It dissolves very easily in hot water, with rise of temperature if previously dehydrated. It is not perceptibly soluble in cold alcohol. Its specific gravity is 1.03845, and its rotatory power $[\alpha] = +213^\circ$. Soluble starch coloured blue by iodine exhibits the same specific rotatory power.

When a solution of dextrin is subjected to the prolonged action of malt-extract, its reducing power is gradually increased, the dextrin being converted first into maltose, and ultimately into dextrose (see SUGARS).

Bondonneau (*Bull. Soc. Chim.* [2], xxi. 50; xxiii. 98) also finds that commercial dextrin cannot be purified from sugar by precipitation with alcohol, but that a perfectly pure product may be obtained by boiling the dextrin with an alkaline solution of cupric chloride. Dextrin thus purified gives with iodine a dark red coloration, which disappears at 40° , but reappears on cooling. It gives no brown colour with caustic soda, no precipitate with ammoniacal silver solution or gold chloride, but is precipitated by baryta-water, and by an ammoniacal solution of lead acetate.

From further experiments, Bondonneau infers that the first product of the action of dilute acid upon starch consists wholly of dextrin (not of a mixture of dextrin and glucose, as asserted by Musculus, *Ann. Chim. Phys.* [3], lx. 203), the dextrin being converted into sugar only at a later stage of the process. By drying the mixture in the cold before saccharification was completed, and extracting the soluble portion with cold water, he found this portion to consist of 13.7 per cent. glucose and 86.3 dextrin, whereas, according to the equation, $4C^6H^{10}O_5 + H^2O = C^6H^{12}O_6 + 3C^6H^{10}O_5$, given by Musculus, which assumes the simultaneous formation of dextrin and glucose, the proportion of the latter should be at least 25 per cent. (*Compt. rend.* lxxx. 972).

Detection of Dextrin.—According to Hager (*Dingl. pol. J.* ccix. 398), an admixture of dextrin with gum-arabic may be detected by laying about 20 lumps of the mixture in a porcelain basin, drenching them with a mixture of equal parts of ferric chloride solution (sp. gr. 1.480 to 1.484) and distilled water, and leaving the liquid to act on them for 30 to 60 seconds. If the basin be then quickly inclined, the lumps of dextrin will roll, while the gum will adhere to the bottom of the basin.

E. Reichardt (*Arch. Pharm.* [3], v. 502) found dextrin in the urine of diabetic patients who had been drinking the waters of Carlsbad, the dextrin making its appearance after the sugar had diminished in quantity or disappeared. It was separated by treating the concentrated urine with potash and alcohol. The resulting precipitate, after washing with alcohol, exhibited the composition of dextrin, reduced Fehling's solution, not immediately, but after some time, was coloured red-brown by iodine, and converted into sugar by heating with dilute sulphuric acid.

On the Estimation of Dextrin in Fermented Liquids, see Béchamp (*J. Pharm. Chim.* [4], xxi. 458; *Chem. Soc. J.* 1876, i. 762).

Isomeric Dextrins. The dextrin which Biot & Persoz obtained by the action of sulphuric acid upon starch (ii. 312) becomes blue with iodine. Béchamp described as dextrin a substance which did not become so coloured, and attributed the reaction of Biot's dextrin with iodine to the presence of soluble starch. According to Nasse, the violet or red tint which dextrin is usually said to give with iodine is a mixture of a blue depending on soluble starch (amidulin), and of a red due to dextrin proper. Béchamp's dextrin, which does not become coloured, is designated by Nasse as *dextrinogen*. Griessmayer finds that filtered starch-paste is gradually converted, first into a dextrin which gives a red colour with iodine (dextrin II), and afterwards into a dextrin (I) which is not coloured by iodine (*2nd Suppl.* 1009). Brücke (*Wien. Akad. Ber.* lxxv. [3], 126) distinguishes the latter as *achromodextrin*, the former as *erythro-dextrin*. He finds that neither erythro-dextrin nor achromodextrin reduces copper solution; and that the reduction of copper by commercial dextrin is due to the presence of sugar. According to Griessmayer, erythro-dextrin has a greater affinity for iodine than starch. Brücke, on the other hand, finds that the blue colour of the starch appears before the red of the erythro-dextrin, when the two are present together, at ordinary temperatures ($18^\circ C.$), though at higher temperatures the affinity of the two substances seems to be equal.

Dextrin may be separated from starch by a modification of Griessmayer's method, viz., precipitation of the starch by means of tannin; but in order to separate the two substances, erythro-dextrin and achromodextrin, from each other, the best method, according to Brücke, is to fractionate with alcohol. First the starch is precipitated, if it has not been previously removed by the tannin, then the erythro-dextrin, and lastly the achromodextrin, which generally carries with it a certain proportion of

sugar. A part of the achromodextrin is also carried down with the erythrodextrin, so that, when only small quantities are present, it is not easy to obtain exact quantitative results.

According to Bondonneau (*Coypt. rend.* lxxxi. 972, 1210), dextrin is susceptible of three isomeric modifications, α , β , γ , which are produced in succession by the action of dilute acids upon starch, and finally converted into glucose. On adding alcohol to the mixture at an early stage of the reaction, a precipitate is formed consisting of two dextrins, one of which (α) is identical with the dextrin produced by roasting, being coloured red by iodine, whereas the second (β) is not altered thereby.* As the action proceeds, the proportion of α -dextrin diminishes, and finally the precipitate formed by alcohol consists wholly of β -dextrin, not coloured by iodine, and identical with the dextrin produced by the action of diastase. The alcoholic solution now contains, in addition to glucose, another non-reducing body, namely γ -dextrin, which is soluble in absolute alcohol, not coloured by iodine, and is very easily converted into glucose by the action of dilute acids. The same bodies (α -dextrin, however, in very small quantity) are formed by the action of diastase. Both α - and β -dextrin are deposited from solutions of 24°–25° Bm. cooled to +1°, in the form of milky masses which become transparent when warmed, and then dissolve completely on agitation. This reaction is not prevented by a small quantity of glucose, but is stopped by a large quantity. Diastase, even at ordinary temperatures, quickly converts α - into β -dextrin, without sensible formation of sugar, the β -dextrin not undergoing any further modification. In warm solutions the α -dextrin disappears almost immediately, and by prolonged action the resulting β -dextrin is almost wholly converted into γ -dextrin and sugar. γ -dextrin has not been obtained pure. Its properties are very much like those of glucosan (ii. 854). Its rotatory power was determined by calculation.

The following table exhibits the most characteristic properties of the three dextrins, compared with those of starch and glucose:

	Rotatory power	Action of iodine	Action of absolute alcohol
Starch	216	Blue	Insoluble
Dextrin, α	186	Red	"
" β	176	Colourless	"
" γ	164	"	Soluble
Glucose	52	"	"

According to O'Sullivan on the other hand, dextrin exhibits exactly the same specific gravity, rotatory power, and other physical properties, whether in its preparation, the action of the acid or of the diastase has been continued till the product gives no colour with iodine, or only till it gives a red colour: hence he infers that dextrin, when properly purified, is one and the same substance, the different reactions with iodine in the product before purification being due to small quantities of other substances (p. 628).

DEXTRONIC ACID, $C^6H^{12}O^9$. According to Reichardt (*Deut. Chem. Ges. Ber.* viii. 1020), this acid is formed from soluble starch by the action of Br and Ag^2O , in the same manner as from dextrin (2nd Suppl. 424).

DEXTROPIMARIC ACID. See PIMARIC ACID.

See SUGARS.

DIABANTITE. Liebe's *Diabantachronnyn* (2nd Suppl. 424). This highly ferruginous variety of chlorite, which gives the green colour to the diabases of the Voigtland and the Frankenwald, occurs also, together with calcium carbonate and silica, in the cavities of the amygdaloidal diabase which forms one of the varieties of trap-rock in the Connecticut valley. A specimen of radiate structure, dark green colour, sp. gr. = 2.79, and hardness = 1, gave by analysis:

%SiO ²	Fe ² O ³	Al ² O ³	FeO	MnO	CaO	MgO	Na ² O	H ² O	
33.24	11.07	2.26	25.11	0.41	1.11	16.51	0.25	9.91	= 99.87
			SiO ²		Fe ² O ³ .Al ² O ³		FeO, MgO, &c.		H ² O
Oxygen-ratio			17.73		5.83		12.66		5.81
Or nearly			4.3		2		6		3

This ratio is that which is required to form a unisilicate of the pyrosclerite group (G. W. Hawes, *Sill. Am. J.* [3], ix. 454).

DIABASE. Microscopical investigations on diabases have been published by J. F. Dathe (*Jahrb. f. Min.* 1874, 640). He divides these rocks into diabases proper and quartz-diabases, both containing plagioclase (probably always oligoclase), augite,

* The dextrins were purified by Bondonneau's method previously described.

titanic iron, magnetic iron ore, iron pyrites and apatite, and the latter also quartz and magnesia-mica. The angite and mica give rise to diabantite (2nd Suppl. 424); calcespar occurs only as a secondary constituent.

A diabase from the south-west foot of the Lion's Head, South Africa, has been analysed by W. F. Hillebrand (*Jahrb. f. Min.* 1874, 460). It forms a vein in the decomposed granite, and consists of wine-yellow augite-grains, plagioclase, magnetic iron ore, small quantities of chlorite and mica, and a green mineral distinguished from chlorite by its ready solubility in hydrochloric acid:

SiO ^a	AlO ^a	FeO ^a	FeO	CaO	MgO	K ² O	Na ² O	H ² O	
52.41	13.04	9.46	8.35	8.36	3.50	1.23	3.24	1.26	± 100.85.

The following analyses of diabases are given in R. v. Drasche's petrographic geological observations on the west coast of Spitzbergen:

1. Diabase separated in voluminous masses, forming a layer 10 meters thick, in the triassic layers of the Tschermak Mountain in the ice-fjord, and consisting of augite, plagioclase, a chloritic mineral, and titanite iron; sp. gr. = 2.98, analysed by Tecla.

2. Diabase from the Goose Islands in the ice-fjord; analysed by G. Lindström.

3. Diabase from the Norway valley on the headland of Saurier-Hook in the ice-fjord, likewise forming a thick layer in the triassic strata; sp. gr. = 2.98.

	SiO ^a	TiO ^a	AlO ^a	FeO ^a	CaO	MgO	MnO ^a	Na ² O	K ² O	X*
(1.)	50.17	trace	14.29	17.87	10.72	5.77	—	0.96	0.18	0.90 = 100.86
(2.)	49.78	2.97†	14.05	14.86	9.44	5.65	0.13	1.70‡	0.18	1.42 = 100
(3.)	50.96	trace	5.23	27.78	10.11	5.39	—	0.4	0.27	0.99 = 100.77

On the Diabases of Nassau, see Sandberger (*Jahrb. f. Min.* 1874, 314; *Jahresb. f. Chem.* 1874, 1303).

On the Diabases of Connecticut, see Hawes (*Sill. Am. J.* [3], ix, 185; *Jahresb. f. Chem.* 1875, 1272).

DIACETONALKAMINE or *Dimethylisoxpropylcarbamine*, $C^6H^{13}NO = C^6H^8.CHOH.CH^2.C \begin{Bmatrix} (CH^3)^2 \\ NH^2 \end{Bmatrix}$, is formed by the action of sodium-amalgam on an alcoholic solution of diacetonnamine (p. 28).

DIACETONAMINE, $C^6H^{12}NO$. See ACETONE-BASES (p. 28).

DIACETONIC ALCOHOL, $C^6H^{12}O^2 = CH^3.CO.CH^2.CO.H \begin{Bmatrix} CH^3 \\ CH^3 \end{Bmatrix}$ (Heintz, *Liebig's Annalen*, clxxviii, 342). This compound is formed by the action of potassium nitrite on diacetonnamine. To prepare it, acid oxalate of diacetonnamine is dissolved in 3 pts. of hot water, and, when the solution has cooled to 5°—whereupon it deposits part of the salt—solid potassium nitrite is gradually added to the mass, with constant stirring. The mixture is immersed in ice-cold water for several days, afterwards heated to 50° or 60°; the oily layer, which separates on the surface and consists for the most part of mesityl oxide, is distilled off as completely as possible; the remaining portion of it is separated from the aqueous solution by means of a tap-funnel; and the aqueous solution, neutralised, if necessary, with potassium carbonate, is shaken up with ether. The ethereal extract thus obtained yields, on treatment in the ordinary way, a syrupy liquid consisting of diacetic alcohol.

This alcohol has a density of 0.9396 at 25°, boils at 163.5°–164.5°, and mixes with water, alcohol, and ether. Treated with sodium, it gives off hydrogen, and yields a sodium-derivative, convertible by treatment with acetyl chloride into an acetyl-derivative. The alcohol does not unite with strong sulphuric acid, but when treated therewith appears to yield mesityl oxide.

DIALDANE, $C^6H^{10}O^2 = \begin{Bmatrix} CH \\ CH \end{Bmatrix} - CH^2 - CHOH - CH^3$. A compound formed by condensation of 2 mols. aldol, $C^4H^8O^2$, with elimination of 1 mol. water, under the influence of hydrochloric acid. (See ALDOL, p. 54.)

DIALDANIC ACID, $C^6H^{10}O^4 = \begin{Bmatrix} CH \\ CH \end{Bmatrix} - CH^2 - CHOH - CH^3$ (Wurtz, *Compt. rend.* lxxxiii, 255, 1259). This acid is formed by heating an aqueous solution of dialdane with silver oxide, or by the action of potassium permanganate at ordinary temperatures; and is obtained in the free state, either from its potassium salt by

* Loss by ignition.

† This high amount of titanite acid is considered by Drasche as doubtful.

‡ Estimated by difference.

means of sulphuric acid and ether, or from the silver salt by hydrogen sulphide. When purified by repeated crystallisation, it forms large colourless, shining, monoclinic crystals; melts at 80° , and boils at 198° under a barometric pressure of 20 mm. It is very soluble in water and in alcohol, soluble also in ether. The aqueous solution has a strong acid reaction, and saturates bases completely. The *potassium salt*, $C^6H^{10}O^4K$, remains, on evaporation of its aqueous solution, as a crystalline deliquescent mass, and separates from boiling alcohol of 98 per cent. in transparent crystals which become turbid on exposure to the air. The *sodium salt*, $C^6H^{10}O^4Na$ (at 125°), is soluble in water and in alcohol, and separates from the latter in transparent plates. The *barium salt* is an amorphous vitreous mass; pulverulent when separated from the alcoholic solution by ether. The *calcium salt*, $(C^6H^{10}O^4)_2Ca$, is a crystalline mass, very soluble in water, but not deliquescent; crystallises from boiling alcohol on cooling in nodules of microscopic needles containing water of crystallisation. The *zinc salt* dissolves easily in water and in alcohol, and remains, on leaving its aqueous solution to evaporate, as an indistinctly crystalline mass; the alcoholic solution leaves it on evaporation as a transparent varnish. The *lead salt* is likewise soluble. The *silver salt*, $C^6H^{10}O^4Ag$, is precipitated as a crystalline pulp on mixing the concentrated solutions of the sodium salt and silver nitrate. It is nearly insoluble in absolute alcohol, and crystallises on cooling from a boiling aqueous solution in tufts of small colourless laminae.

DIALLAGÉ. A black diallage, sp. gr. 3.365, from the gabbro of Monte Monzoni, analysed by G. vom Rath (*Zeitschr. geol. Ges.* xxvii. 371) was found to contain 45.88 per cent. SiO_2 , 5.10 Al_2O_3 , 12.62 Fe_2O_3 , 20.30 CaO , and 13.81 MgO = 97.71.

On the diallagite-olivine rock of Mohsdorf in Saxony, see Dathe (*Jahrb. f. Min.* 1876, 225; *Chem. Soc. Jour.* 1876, ii. 388).

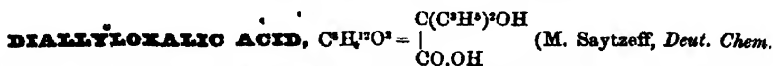
DIALLYL-CARBINOL, $(C^3H^5)_2CHOH$ (M. Saytzeff, *Liebig's Annalen*, clxxxv. 129; *Ber.* ix. 1600). This alcohol is formed by the action of zinc on a mixture of allyl iodide and ethyl formate. The mixture must be cooled at the commencement of the reaction, which is completed by addition of water. The crude product consists of diallyl, small quantities of a high-boiling product, and diallyl-carbinol. The formation of the latter may be represented by the equation:



Diallyl-carbinol boils at 151° (corr.), unites with bromine, forming a tetrabromide, and with acetic anhydride, producing an acetic ether, which again forms a tetrabromide convertible by silver acetate into the acetic ether of a pentatomic alcohol, $C^5H^{11}(O.C^2H^5)_2$. This ether boils at 169.5° (corr.), has a sp. gr. of 0.919 at 0° ; 0.902 at 150° , and is converted by saponification with alcoholic hydrochloric acid into an anhydride of the corresponding alcohol, $C^5H^{11}\left\{ \begin{smallmatrix} O \\ (OH)^2 \end{smallmatrix} \right.$.

Diallylcarbinyll Chloride or *Chloranhydride* (monochlorheptene), $C^5H^{11}Cl = (C^3H^5)_2.CHCl$, is formed when pentachloride of phosphorus acts on the carbinol; it boils between 140° and 145° , but appears in so doing to lose the elements of hydrochloric acid and become partially converted into the hydrocarbon, C^5H^{10} (heptene), or a polymeride of higher boiling point. This hydrocarbon is readily formed, together with its polymerides, by the action of alcoholic potash on the chloride. It boils at 115° , and readily combines with 6 atoms of bromine, forming the compound $C^5H^{10}Br^6$, which probably has the constitution $CH^2Br-CHBr-CHBr-CHBr-CH^2-CHBr-CHBr$, and may be regarded as the hexbromhydrin of a hexatomic alcohol, and by suitable treatment may possibly yield a homologue of mannite.

On oxidation with potassium dichromate and sulphuric acid, diallyl carbinol yields formic acid and carbon dioxide; no acetic acid is produced, and nothing else has been isolated from the product of the reaction: whence it follows that the structure of the allyl groups in the carbinol is $CH^2=CH-CH^2-$, and not $CH^2-CH=CH-$, since in the latter case acetic acid must have been formed. Hence, and from its mode of formation, the formula of the carbinol must be:



The ethylic ether of this acid is produced by the action of zinc on a mixture of ethyl oxalate and allyl iodide:



Ethyllic diallyloxalate is a colourless liquid of faint ethereal odour, boiling at 213.6° . Its sp. gr. is 0.9873 at 0° , and 0.9718 at 18° . When heated with caustic baryta, it is converted into barium diallyloxalate, from which the free acid is obtained by decomposition with sulphuric acid.

Diallyloxalic acid crystallises in radiated groups of needles, or in long bundles of microscopic rectangular crystals. It dissolves easily in alcohol and ether, sparingly in water; melts at 48.6° , and distils without decomposition.

The *barium salt*, $(C^2H^{10}O^3)^2Ba$, crystallises in delicate needles, which dissolve easily in water and alcohol. The *zinc salt*, $(C^2H^{10}O^3)^2Zn + 14H^2O$, formed by neutralising the acid with zinc carbonate, resembles the barium salt. The *lead salt*, $(C^2H^{10}O^3)^2Pb + 2H^2O$, crystallises from concentrated solutions in stellate groups of monoclinic crystals. It melts at 100° , slowly giving off its water of crystallisation. The calcium, ammonium, sodium, and silver salts have also been prepared. Solutions of the last turn brown, even in the dark and in a vacuum.

Tetrabromodiallyloxalic acid, $C^2H^{12}Br^4O^4$, is a crystalline substance, formed on mixing a cooled solution of diallyloxalic acid in ether with a slight excess of bromine.

DIALURATES. Liebig & Wöhler, by the action of reducing agents on alloxan and by that of ammonium hydrosulphide on uric acid dissolved in nitric acid, obtained a salt having the composition $C^2H^2(NH^2)^2N^2O^4$, which they designated as ammonium dialurate; and Strecker obtained the corresponding potassium salt by the action of potassium cyanide on aqueous alloxan (ii. 315). According to Menachutkin, however (*Liebig's Annalen*, clxxxii. 70), these salts are derived from salts of another series, having, according to analysis, the general formula, $C^2H^2M^2N^2O^4$ (M being univalent). Of this latter series the ammonium, potassium, sodium, and barium salts have been examined, but their molecular constitution is not yet made out. Both series of salts are provisionally called dialurates.

Ammonium dialurate forms the starting point for the preparation of other dialurates. When prepared either by Liebig and Wöhler's process (by the action of nitric acid on uric acid and subsequent reduction of the product by ammonium sulphide), or by Strecker's process (action of ammonia on alloxan in presence of hydrocyanic acid), it crystallises in long needles, agreeing approximately in composition with the formula, $C^2H^2(NH^2)^2N^2O^4$. It is very unstable, and when crystallised repeatedly from hot water in presence of ammonium carbonate, is gradually transformed into microscopic prisms, which are perfectly constant in composition, and agree with Liebig and Wöhler's formula, $C^2H^2(NH^2)^2N^2O^4$. The latter salt acquires a rose-red colour in the air. It dissolves sparingly in boiling water, being immediately transformed into the salt $C^2H^2(NH^2)^2N^2O^4$. The solution gives by double decomposition salts of the same series.

Potassium dialurate, $C^2H^2K^2N^2O^4$, obtained by mixing boiling saturated solutions of the ammonium salt and potassium acetate, crystallises in small needles, which turn rose-red in the air. It dissolves very sparingly in boiling water, and is completely decomposed on prolonged boiling therewith. By crystallisation in presence of much potassium carbonate it is transformed into a granular precipitate having the formula $C^2H^2KN^2O^4$, and identical with Strecker's salt. The latter, when dissolved in boiling water, is immediately reconverted into the salt $C^2H^2K^2N^2O^4$, in this respect resembling the ammonium salt.

Sodium dialurate, $C^2H^2Na^2N^2O^4$, is obtained in the same way as the potassium

water,
molecule

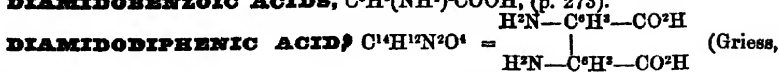
$C^2H^2Na^2N^2O^4$. It does not appear to be convertible into the salt $C^2H^2NaN^2O^4$.

Barium dialurate, $C^2H^2Ba^2N^2O^4$, like the sodium salt, exists in one form only. It is obtained as a white crystalline precipitate by adding barium chloride to a dialurate of either series. It is nearly insoluble in water.

Urea dialurate, $CH^2N^2O.C^2H^2N^2O^4$.—When a warm aqueous solution of dialuric acid (prepared by the action of tin and hydrochloric acid on alloxan) is mixed with urea, and left at rest in a closed vessel, stellate crystals separate out, which, after drying in the exsiccator, have the composition of urea dialurate. This compound is sparingly soluble in water, has an acid reaction, and gives a fine blue coloration with ferric chloride and ammonia. It may be preserved without decomposition, but when heated to 160° it gives off water and turns red (E. Mulder, *Deut. Chem. Ges. Ber.* vi. 1004).

DIAMIDOBENZENES, $C^6H^4(NH^2)^2$. See BENZENE-DERIVATIVES (p. 210).

ACID, $C^6H^4(NH^2)^2(SO^2H)$, (p. 228).

DIAMIDOBENZOIC ACIDS, $C^6H^3(NH^2)^2COOH$, (p. 273).

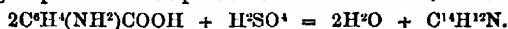
Deut. Chem. Ges. Ber. vii. 1609). The *meta*-modification of this acid, ($CO^2H : NH^2 = 1 : 3$), is formed by boiling metazofybenzoic acid (p. 277) for a considerable time with tin and hydrochloric acid. It is isolated from the product in the ordinary way; freed from simultaneously formed amidobenzoic acid by exhaustion with hot water, in which it is but slightly soluble; and further purified by repeated solution in hydrochloric acid, decoloration with animal charcoal, and separation from the decolorised liquid with ammonia and acetic acid. It may also be prepared by

boiling the isomeric compound metahydrazobenzoic acid, $\begin{array}{c} HN-C^6H^4-CO^2H \\ | \\ HN-C^6H^4-CO^2H \end{array}$ with hydrochloric acid. For the description of its properties and compounds, see p. 277.

Orthodiamidodiphenic acid appears to be formed in like manner by the action of boiling hydrochloric acid on orthohydrazobenzoic acid.

DIAMIDONAPHTHALENE. See NAPHTHALENE.

DIAMIDOSULPHOBENZIDE-DICARBONIC ACID (Michael a. Norton, *Deut. Chem. Ges. Ber.* x. 580-583). The substance thus named is obtained by the action of fuming sulphuric acid on paramidobenzoic acid at $170^\circ-190^\circ$:



It dissolves easily in hot water, and separates on cooling in tufts of rose-red crystals, which dissolve sparingly in alcohol and ether, very slightly in chloroform. It dissolves readily in alkalis, forming neutral, easily soluble salts.

The *ammonium salt* crystallises in thin laminae; the *potassium salt* in small needles. The *barium salt* is very freely soluble in water. The *lead salt*, obtained by precipitation, is white, and nearly insoluble in water. The *silver salt*, $C^{14}H^{12}Ag^2N^2SO^4$, is precipitated in small white laminae, on adding silver nitrate to the ammonium salt. It is insoluble in cold water, and gradually turns brown in the light.

DIAMIDOXYSULPHOBENZIDE. See OXYSULPHOBENZIDE.**DIAMIDOTOLUENE.** See TOLUENE.

DIAMINES. A series of these bodies occurring, as secondary products, in the manufacture of methylaniline, has been described by Hofmann a. Martins (*Deut. Chem. Ges. Ber.* vi. 346). One portion of the basic oils set free by lime from the products of the reaction, which takes place in the autoclaves, may be volatilised by steam, but another and a considerable portion cannot be thus volatilised. This latter portion consists of oils solidifying at a low winter temperature to a buttery mass, which may be freed from adhering oil by pressure between linen, and crystallised from boiling alcohol. The crystals thus obtained are a mixture of different bases, one of which, in consequence of its superior tendency to crystallise, may easily be separated from the rest. For this purpose, the pressed product is dissolved in hydrochloric acid, and the solution, separated from tarry matters, is precipitated by potash, whereby a brown liquid is separated which solidifies after a few seconds to a crystalline pulp. This pulp is pressed and dissolved in boiling alcohol, and the crystals which separate on cooling are purified by recrystallisation. These crystals melt at 83° , are insoluble in water, slightly soluble in cold, easily in boiling alcohol; also in ether and carbon bisulphide. The pure crystals, which have the composition $C^{10}H^{12}N^2$, are well-defined needles having a splendid silky lustre. The *hydrochloride*, $C^{10}H^{12}N^2 \cdot 2HCl$, is very soluble in water. The *hydrobromide*, $C^{10}H^{12}N^2 \cdot 2HBr$, crystallises in thin rhombic laminae. The *hydroiodide* forms large laminae. The *mercuric compound* is a crystalline precipitate having the composition $C^{10}H^{12}N^2 \cdot 2HCl \cdot 3HgCl^2$.

On heating the base to 100° with methyl iodide, a white gypsum-like mass is formed which has the composition $C^{10}H^{12}N^2 \cdot 2CHI^2$, and is decomposed by boiling water, 1 mol. methyl iodide being given off, and an iodide being left, which crystallises in white flattened needles having the composition $C^{10}H^{12}N^2 \cdot CHI^2$. This iodide dissolves easily in hot alcohol, is precipitated from its aqueous solution by alkalis, and is converted by silver oxide into a strongly basic hydroxyl-compound. The base $C^{10}H^{12}N^2$ is therefore a tertiary diamine, and it may be represented by the formula $C^3H^3(OH^2)^3 \cdot [N(OH^2)]^2$, that is to say, as benzidine, $C^6H^4(NH^2)^2$, in which three hydrogen-atoms of the nucleus, as well as the four hydrogen-atoms of the side-chains,

NH^2 , are replaced by methyl. It might also be regarded as $\begin{array}{c} [C^3H^3(OH^2)^3] \\ (CH^3)^2 \\ (CH^3)^2 \end{array} N^2$, that is, as consisting of 2 mols. of xylylidine, $C^6H^4(NH^2) \cdot (CH^3)^2$, linked together by the

methylene group, CH_2 , and having the two hydrogen-atoms of the ammonia-residue, NH_2 , replaced by methyl, just as in ethylene-diphenyl-diamine, $[(\text{C}^6\text{H}_5)(\text{C}^6\text{H}_5)\text{H}]_2\text{N}_2$, 2 mols. of aniline may be regarded as linked together by ethylene. The base, $\text{C}^{10}\text{H}_{16}\text{N}_2$, does, in fact, exhibit in its chemical relations a very close analogy to ethylene-diamine, as, for example, in its power of uniting with 1 mol. of methyl iodide.

Action of Nitrous acid on Diamines (Ladenburg, *Deut. Chem. Ges. Ber.* ix. 219).—The diamines of the meta-series are converted by nitrous acid into amidazo-compounds. Thus, ordinary diamidobenzene or meta-phenylene-diamine, $\text{C}^6\text{H}_3(\text{NH}_2)_2$, is converted into triamidazobenzene (phenylene-brown), and similar compounds are obtained from para-ortho-diamido-toluene, $\text{C}^6\text{H}_3(\text{NH}_2)_2$, and nitropara-ortho-diamido-toluene. (See AMIDOTOLUENES under TOLUENE.)

The diamines of the ortho-series behave quite differently. When para-meta-diamidotoluene, $\text{C}^6\text{H}_3(\text{NH}_2)_2$, melting at 89° , is dissolved in dilute sulphuric acid, potassium nitrate added drop by drop to the cooled solution, and the liquid

then boiled, amidazotoluene, $\text{C}^6\text{H}_3\text{N}_2 = \begin{array}{c} \text{H}^3\text{C} \\ \diagup \quad \diagdown \\ \text{H}^3\text{N} \end{array} \begin{array}{c} \text{N} \\ \diagdown \quad \diagup \\ \text{N} \end{array}$, is formed, crystallising from hot toluene in large transparent prisms melting at 83° and boiling at 323° .

Orthodiamidobenzene (m. p. 99°) yields in like manner amidazophenylene, $\text{C}^6\text{H}_3\text{N}_2$, or $\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{H}^3\text{N} \end{array} \begin{array}{c} \text{N} \\ \diagdown \quad \diagup \\ \text{N} \end{array}$, which crystallises from a mixture of benzene and toluene in pearly needles melting at 98.5° .

A third body belonging to this group is nitramidazophenylene (azonitro-phenylic acid), $\text{C}^6\text{H}_3(\text{NO}_2)\text{N}_2$ (iv. 484), obtained by the action of nitrous acid on nitrophenylene-diamine.

DIAMOND. See CARBON (p. 402).

DIAMYL or DI-ISOPENTYL, $\text{C}^{10}\text{H}_{22} = \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3) \\ | \\ \text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3) \end{array}$. This hydro-

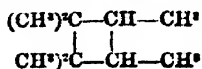
carbon, which was first obtained by Frankland by the action of zinc-amalgam on amyl-iodide, afterwards by Wurtz, by heating the same iodide with sodium, has recently been further studied by Grimshaw (*Chem. Soc. Jour.* 1877, ii. 260, 687), who prepares it by gradually mixing amyl bromide (30 grams) with sodium (50 grams), and heating the mixture for six hours to 140° – 150° . The product, purified by fractional distillation, boils at 168° under a barometric pressure of 751 mm. (Frankland's product boiled at 155° ; Wurtz's at 158° .)

Chlorine passed into boiling diamyl forms a chloride boiling at 198° – 213° , and, by heating this chloride to 160° – 170° with lead acetate and acetic acid, an acetate is obtained in the form of a colourless mobile liquid having a pleasant fruity odour, and boiling at 198° – 215° . On mixing the acetate with excess of caustic potash and a little water, leaving the mixture to itself for twenty-four hours, and then heating it to boiling for six hours in a reflux apparatus, two alcohols are produced, one of which boils at 202° – 203° , the other at 211° – 213° . Both are liquids having a faint colour and a pleasant odour. On heating a mixture of the two alcohols with potassium dichromate and dilute sulphuric acid, and distilling the product, a watery and an oily distillate were obtained, the former containing acetic acid, and the latter yielding, by further oxidation and distillation, an acid whose silver salt was found to contain 63.66 per cent. silver; apparently, therefore, a mixture of acetate (64.66 per cent. Ag) and valerate (51.67 per cent.).

DIAMYL CARBOXYBENZONIC ACID, $\text{C}^{10}\text{H}_{16}\text{O}_2$. An acid, the potassium salt of which is formed by heating deoxybenzoin with a solution of potash in amyl alcohol (p. 628).

DIAMYLENE, C^8H_{16} . When ordinary amylene or trimethyl-ethylene (h.p. 35°) prepared by dehydration of tertiary amyl alcohol, $[\text{CH}_3-\text{CH}_2-\text{COH}(\text{CH}_3)]_2 = \text{H}_2\text{O} + \text{CH}_3-\text{CH}=\text{C}(\text{CH}_3)_2$, is briskly agitated in a glass tube with moderately strong sulphuric acid (sp. gr. 1.64) the tube being well cooled, it is converted into a diamylene, which boils at 154° – 156° , and appears from its oxidation-products—acetic acid, carbon dioxide, and diamylene oxide—to be identical with ordinary diamylene (2nd Suppl. 64), (Wichnegradsky, *Deut. Chem. Ges. Ber.* viii. 434).

The structure of ordinary diamylene may therefore be represented by the formula



DIANILINE-HYDRIN—DIAZO-COMPOUNDS.

$C^6H^5N^2O = C^6H^5(OH)(C^6H^5N)^2$, is formed by heating dichlorhydrin (1 mol.) with excess of aniline (4 mols.) to 120° – 130° for sixteen to twenty hours. It crystallises in white needles soluble in dilute acids. The solutions decompose when heated, or after long standing. The *platindichloride* forms fine yellow-red crystals (Claus & Dörrenberg, *Deut. Chem. Ges. Ber.* viii. 242).

See MORPHINE.

See BIURET (p. 332).

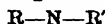
See MELAMINE.

DIATREBIC ACID. See TREBIC ACID.

DIAZO-COMPOUNDS. The view generally entertained of the constitution of these compounds, is that proposed by Kekulé (1st *Suppl.* 209), according to which they all contain the diazo-group $-N=N-$, united on the one side with the univalent benzene-residue C^6H^5 , and on the other side with another univalent group; thus,

Diazobenzene Nitrate	$C^6H^5-N=N-NO^2$
Diazobenzene Sulphate	$C^6H^5-N=N-SO^2H$
Diazobenzene Chloride	$C^6H^5-N=N-Cl$
Diazobenzene Bromide	$C^6H^5-N=N-Br$
Diazobenzene-potassium	$C^6H^5-N=N-OK$
Diazobenzene-silver	$C^6H^5-N=N-OAg$
Diazo-amidobenzene	$C^6H^5-N=N-NH-C^6H^5$
Free Diazobenzene	$C^6H^5-N=N-OH?$

Another view, originally suggested by Strecker (*Deut. Chem. Ges. Ber.* iv. 786), and further developed by Erlenmeyer (*ibid.* vii. 1110), represents them as ammonium compounds constituted according to the general formula,

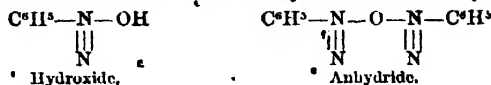


diazobenzene nitrate, for example, being related to aniline nitrate (amidobenzene nitrate) in the following manner:



that is to say, the reaction of nitrous acid on aniline nitrate consists in the replacement of 3 hydrogen-atoms in the phenyl-ammonium group by 1 atom of nitrogen, the nitric acid residue as well as the phenyl remaining united with quinquivalent nitrogen-atoms of phenyl-ammonium.

Free diazobenzene is either an ammonium hydroxide or its anhydride; thus,



The compounds of diazobenzene with metals, potassium for example, and diazo-amidobenzene, may be represented respectively by the formulæ:



while the perbromide and diazobenzenimido may be represented as follows:



For Griess's formulæ of the diazo-amido compounds, see p. 216.

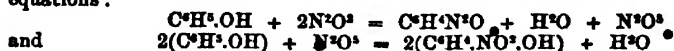
DIAZO-ANTHRAQUINONE. See ANTHRAQUINONE (p. 98).

DIAZO-CRESOL. See 2nd *Suppl.* p. 932.

DIAZO-ORTHOAMIDOPARATOLUENESULPHONIC ACID. See TOLUENE-SULPHONIC ACIDS.

DIAZO-OXYBENZOIC ACID. See BENZOIC ACID DERIVATIVES (p. 277).

DIAZOPHENOL, $C^6H^4N^2O$. This compound is formed, together with the two crystallised mononitrophenols, when gaseous nitrogen trioxide is passed into an ethereal solution of phenol. The reaction may be represented by the following equations:



The diazophenol separates in the form of a well crystallised nitrate (Wesselsky, *Wien. Akad. Ber.* 1875, p. 9).

DIAZOPHENYL-SULPHURIC ACID. See PHENYL-SULPHURIC ACID.

DIBENZAMIDE, $NH(C^6H^5O)^2$. See BENZAMIDE.

DIBENZOYL-ANTHRACENIC ACID. See ANTHRACENIC ACID (2nd Suppl. 88).

DIBENZOYL-BENZENE and **DIBENZHYDRYL-BENZENE.** See DIBENZYL-BENZENE (p. 639).

DIBENZOYL-BENZOIC ACID. See BENZOYL-BENZOIC ACID (p. 312).

DIBENZOYL-CODINE. See CODINE under OPIUM-BASES.

DIBENZOYL-NAPHTHOLS. See NAPHTHOLS.

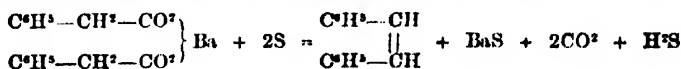
DIBENZOYL-FLUORESCIN. See FLUORESCIN.



heating barium phenylacetate (α -toluate), $(C^6H^5CO^2)^2Ba$, with sulphur, according to the equation:



which, as Radziszewski has shown (*Deut. Chem. Ges. Ber.* vii. 143), represents in general the action of sulphur on the barium salts of aromatic acids. According to the same chemist, however (*ibid.* viii. 758), the hydrocarbon formed in the case under consideration, is not dibenzyl but stilbene, $C^{12}H^{12}$, the reaction being attended with evolution of hydrogen sulphide as well as carbon dioxide; thus:



This result is doubtless to be attributed to the action of sulphur at high temperatures on the dibenzyl formed in the first instance.

Dibenzyl is formed, together with benzaldehyde, deoxybenzoin and water, by subjecting benzoin to distillation, or passing its vapour through a red-hot tube (Zinin, *Deut. Chem. Ges. Ber.* vi. 489). It is also formed by heating toluene, C^7H^8 , with hydriodic acid and red phosphorus (Barbier, *Compt. rend.* lxxviii. 1772).

Crystalline Form.—Dibenzyl crystallises in monoclinic prisms having the following axial ratio:

$$a \text{ (clinod.)} : b \text{ (orthod.)} : c \text{ (principal axis)} \\ 1.27026 : 1 : 1.91583$$

$$\text{Angle } \alpha : \beta = 101^\circ 32' 50''.$$

Combination: $\infty P. - P\infty . P\infty . 0P. P(\infty)$. Angle: $-P\infty : \infty P = 122^\circ 50'$. $P\infty : \infty P = 120^\circ 5'$; $-P\infty : P\infty = 113^\circ 20'$; $\infty P : \infty P = 102^\circ 26'$. Twins occur, having the positive hemidome for twin- and combination-plane (G. vom Rath, *Deut. Chem. Ges. Ber.* v. 622).

Decompositions.—1. By Heat. Dibenzyl, when heated, is completely resolved into stilbene and toluene, $2C^{12}H^{12} = C^{14}H^{12} + 2C^7H^8$ (Barbier, *Compt. rend.* lxxviii. 1769).

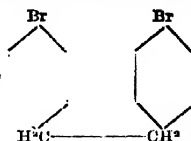
2. By Oxidation.—Dibenzyl is carbons of the aromatic group.

(Liebig's *Annalen*, cxxvii. 257); osmium dichromate and sulphuric acid, obtained only small quantities of benzoic acid. W. Leppert, however (*Deut. Chem. Ges. Ber.* ix. 14), finds that when a solution of dibenzyl in glacial acetic acid is treated with chromic acid, very considerable oxidation

takes place, the whole mass quickly turning green; the complete oxidation of the dibenzyl, however, requires a long time.

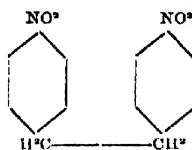
The product of this oxidation is benzoic acid, without previous formation of deoxybenzoïn or benzile, which, according to Radziszewski, may be regarded as intermediate products of the oxidation of dibenzyl (2nd Suppl. 176). Hence it must be inferred that in the oxidation of dibenzyl, $C^6H^5-CH^2-CH^2-C^6H^5$, the molecule is first split in halves, and the CH^2 in each half is then oxidised to $COOH$.

Constitution of Dibenzyl-derivatives.—Dibromodibenzyl, $C^{12}H^{12}Br^2$ (v. 871), treated with chromic acid mixture, is oxidised to parabromobenzoic acid; it must therefore contain 1 atom of bromine in each of its benzene nuclei, this bromine-atom occupying the para-position relatively to the CH^2 group

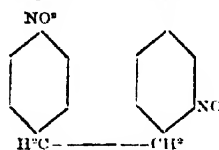


Dinitrodibenzyl, $C^{12}H^{12}(NO^2)^2$. Of this compound there are two modifications, one melting, according to Stölling a. Fittig (v. 871), at $166^\circ-167^\circ$, the other called isodinitrodibenzyl, at $74^\circ-75^\circ$. According to Leppert (*Deut. Chem. Ges. Ber.* ix. 14), the former, when purified by repeated crystallisation from alcohol, forms long, heavy, white needles melting at 178° .

Both modifications, when dissolved in glacial acetic acid and oxidised by chromic acid, yield paranitrobenzoic acid as sole product of oxidation, but the quantity of this acid obtained from isodinitrodibenzyl is very much smaller than that which is obtained by oxidation of the other modification. Hence it appears most probable that dinitrodibenzyl is constituted like dibromodibenzyl, having a nitro-group in each benzene-nucleus occupying the para-position relatively to the CH^2 group, and that in isodinitrodibenzyl, one of the nuclei has its side chains arranged in the same manner, while in the other, the NO^2 and CH^2 are relatively in the ortho-position: thus



Dinitrodibenzyl.



Isodinitrodibenzyl.

The oxidation of this latter modification would then yield in the first instance a mixture of para- and ortho-nitrobenzoic acids, and, taking into account the comparative instability of many ortho-derivatives of benzene, it may be supposed that the ortho-nitrobenzoic acid undergoes further oxidation.

Diamido and Isodiamidodibenzyl are similar in constitution to the two nitro-derivatives (Leppert).

Dihydroxydibenzyl, $C^{12}H^{12}O^2 = C^6H^4(OH).CH^2.CH^2.C^6H^4(OH)$, is formed, together with paraoxybenzoic acid, by prolonged fusion of dibenzyl-disulphonic acid with potash (p. 332). It forms white shining laminae, nearly insoluble in cold, but easily soluble in boiling water (Kade, *Deut. Chem. Ges. Ber.* vii. 239).

DIBENZYL-ACETIC ACID, $CH(CH^2.C^6H^5)^2-CO^2H$. See BENZYL-ACETIC ACIDS (p. 317).

DIBENZYL-ACETOACETATE, ETHYLIC, $C^{20}H^{22}O^4 = CH^2.CO.O(CH^2.C^6H^5)^2-CO.O.C^2H^5$, formed by the action of benzyl chloride on the sodium derivative of ethylic benzylacetoacetate, $CH^2.CO.CNa(CH^2.C^6H^5)-CO.O.C^2H^5$ (p. 317), is a viscid oil which decomposes when distilled (Ehrlich, *Deut. Chem. Ges. Ber.* viii. 1035).

DIBENZYL-BENZENE, $C^{20}H^{18} = C^6H^4(C^6H^5)^2 = C^6H^4 \begin{matrix} \diagup CH^2-C^6H^5 \\ \diagdown CH^2-C^6H^5 \end{matrix}$ (Zincke, *Deut. Chem. Ges. Ber.* vi. 119; ix. §1). Two modifications, α and β , of this hydrocarbon are formed, together with monobenzylbenzene, $C^6H^5-CH^2-C^6H^5$, or diphenylmethane, when benzyl chloride is heated with benzene and zinc powder. The diphenylmethane constitutes the lower-boiling portion of the product, and after it has passed over, the temperature quickly rises beyond the range of the mercurial thermometer, and an oily liquid distills over which soon solidifies to a crystalline pulp.

The solid portion of this distillate consists chiefly of the two dibenzyl-benzenes.

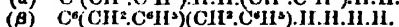
The α -modification crystallises from dilute alcohol in large transparent laminae or oblique plates, melting at 86° and solidifying again at 78° . When slowly cooled it remains amorphous and transparent, but becomes crystalline at once on touching and heating it gently. It is not very soluble in ether, but dissolves readily in benzene, chloroform, and carbon sulphide. The β -modification dissolves more readily in ether and the other solvents, and crystallises from hot alcohol in thin, long, flat, silky needles, melting at 78° and solidifying at 68° . When cooled down slowly, it behaves like its isomeride. Neither of the two combines with picric acid, but the two combine together, crystallising from alcohol in hard, brilliant, acicular prisms, melting at 83° – 84° . This compound, or perhaps isomorphous mixture, is not decomposed by recrystallisation from alcohol, and can be resolved in its constituents only by repeated treatment with ether.

The two dibenzyl-benzenes are converted by oxidation with chromic acid and acetic acid, or with potassium chromate and sulphuric acid, into bodies having the composition $C^{12}H^{10}O^2$; the oxidation taking place in such a manner that the two CH^2 groups in the molecule are converted into CO groups, the product being a mixture of two isomeric double ketones, or dibenzoyl-benzenes:



Together with these ketones, there are formed small but distinctly recognisable quantities of para- and ortho-benzoyl-benzoic acids (p. 310), the α -modification of dibenzyl-benzene yielding the para, and the β -modification the ortho-benzoyl-benzoic acid:

The former is therefore the 1 : 4, and the latter the 1 : 2 modification of dibenzyl-benzene.

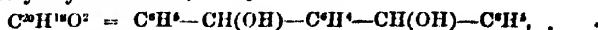


α or para-dibenzyl-benzene is also produced, according to Baeyer (*Deut. Chem. Ges. Ber.* vi. 220), together with monobenzyl-benzene, by the action of sulphuric acid on a mixture of benzene and methylal. Baeyer did not actually observe the formation of the β -modification, but he obtained large spicular crystals probably identical with those above described as consisting of a mixture of the two modifications.

α -Dibenzoyl-benzene, $C^{12}H^{10}O^2$, is best obtained by oxidation with chromic and acetic acids, the yield being about 80–90 per cent. of the calculated quantity; easily also by the action of nitric acid (Wehren, *Deut. Chem. Ges. Ber.* ix. 309). It is insoluble in water, slightly soluble in cold, easily in hot alcohol, and separates therefrom on cooling in flat shining needles or laminae. From ether, in which it is also but sparingly soluble, it separates in large prismatic needles. In chloroform and glacial acetic acid it dissolves more freely, separates from chloroform in large wedge-shaped pointed crystals, from hot glacial acetic acid in broad shining needles. It melts at 159° – 160° , and decomposes at higher temperatures, emitting an odour of diphenyl.

β -Dibenzoyl-benzene is prepared like the α -compound, but the yield is much smaller, a large portion of the dibenzyl-benzene being decomposed, with evolution of carbon dioxide. It is more soluble in the above-mentioned solvents than the α -modification, and exhibits greater tendency to crystallise. From alcohol, ether, or chloroform, it separates in large rectangular plates, having a faint yellow colour, and grouped like steps. It melts at 145° – 146° , and does not volatilise without decomposition (Zincke).

α . Dibenzhydriol-benzene,

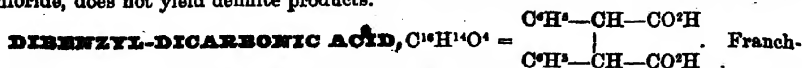


is an alcoholic compound obtained by the action of sodium amalgam and alcohol on α -dibenzoyl-benzene. It crystallises from alcohol in glistening needles, melts at 171° , dissolves readily in ether, chloroform, and benzene, and is reconverted by chromic acid into α -dibenzoyl-benzene. Heated to 150° – 160° with acetic anhydride, it is converted into the diacetate, $C^{12}H^8(O^2C^2H^3O)^2$, which crystallises in square plates, melting at 113° – 114° , and dissolving easily in hot, less easily in cold alcohol, ether, and glacial acetic acid. The monoacetate, $C^{12}H^9(OH)(O^2C^2H^3O)$, produced by heating the alcohol with

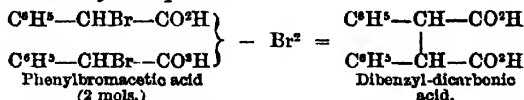
glacial acetic acid, forms nodular groups of crystals melting at 94° – 97° . The dibenzoate also forms nodules melting at 185° – 186° (Wehren, *loc. cit.*)

The corresponding tetrachloride, $C^{12}H^4Cl^4 = C^6H^5.CCl^2.O^2C^2H^3.CCl^2.C^6H^5$, is easily formed by treating α -dibenzoyl-benzene with phosphorus pentachloride. The action takes place quietly at 150° , and the resulting ketonic chloride crystallises easily from ether free from water and alcohol, in tabular crystals, apparently monoclinic, having a vitreous lustre, and melting at 91° – 92° . It is very unstable, and is reconverted into dibenzoyl-benzene by warming with water, alcohol, and glacial acetic acid (Wehren).

β . Dibenzoyl-benzene, treated with sodium-amalgam or with phosphorus pentachloride, does not yield definite products.



imont (*Deut. Chem. Ges. Ber.* v. 1048) obtained this acid in attempting to prepare phenylmalonic acid from phenylacetic (α -toluic) acid. This phenylated acid heated with bromine yields phenylbromacetic acid, the ethylic ether of which, heated in sealed tubes in a water-bath with alcoholic potassium cyanide, yields potassium bromide and a slightly coloured liquid, which, when heated with potash, gives off large quantities of ammonia; and on evaporating this solution to dryness, after prolonged heating, and treating the residue with excess of hydrochloric acid, a mixture of gases smelling of hydrocyanic acid is evolved, and an acid is precipitated, which, when crystallised from boiling water, and then from hydrochloric acid, in which it is much more soluble, has the composition $C^6H^5O^2$, or rather $C^{10}H^{10}O^4$. Its formation from phenylbromacetic acid may be represented by the equation:

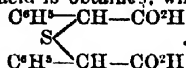


The bibasic nature of this acid is confirmed by the composition of its barium and silver salts, and by the existence of a monethylic ether.

Benzyl-dicarbonic acid crystallises from dilute hydrochloric acid with 1 molecule of water; from benzene in small shining crystals, which soon become dull. The acid crystallised from hydrochloric acid melts at 182° , then solidifies, and afterwards melts at 222° ; the acid crystallised from benzene melts at 169° – 170° , then solidifies, and afterwards melts at 222° . Monethylic dibenzyl-dicarbonate crystallises from ether, and melts at 140° .

Calcium dibenzyl-dicarbonate, distilled with excess of quicklime, yields a crystalline distillate, which, by repeated pressing and recrystallisation from alcohol, is resolved into dibenzyl, $C^{10}H^{10}$ (m. p. 51°), and stilbene, $C^{14}H^{12}$ (mp. 118°), the latter being formed from dibenzyl by the action of heat.

By heating ethylic phenylbromacetate with potassium monosulphide, a well crystallised sulphuretted acid is obtained, which appears to have the constitution represented by the formula



DIBENZYL-DISULPHONIC ACID. See BENZYL-SULPHONIC ACIDS (p. 322).

DIBENZYL-FLUORESCIN. See FLUORESCIN.

DIBENZYL KETONE, $C^{10}H^{10}O = CO < \begin{array}{l} CH^3.C^6H^5 \\ CH^3.C^6H^5 \end{array}$. This ketone, oxidised by chromic acid mixture, yields, not phenyl-acetic acid, but its products of oxidation, benzoic and acetic acids.

Liquid dibenzyl ketone crystallises on addition of sodium bisulphite; the crystals, however, consist not of a double salt, but of pure dibenzyl ketone melting at 30° , and boiling at 320° – 321° (Popoff, *Deut. Chem. Ges. Ber.* vi. 560).

DIBENZYL-METHANE, $C^{10}H^{10} = CH^2(CH^3.C^6H^5)_2$, is formed, together with dibenzyl-phosphonic acid, $C^{10}H^{10}PO^3$, by heating dibenzyl ketone to 180° with hydriodic acid and amorphous phosphorus. The crude viscid product solidifies, on addition of caustic soda, to a crystalline pulp from which the hydrocarbon may be extracted by ether. Dibenzyl-methane boils for the most part between 290° and 300° , and does not solidify in a freezing mixture (Graebe, *Ber.* vii. 1623).

DIBENZYL-PHOSPHINE, $PH(C^6H^5)_2$. See PHOSPHINES (2nd Suppl. 956).

DIBENZYL-PHOSPHONIC ACID, $C^{10}H^{10}PO^3 = C^{10}H^{10}.PO(OH)_2$. This acid, which forms about two-thirds of the crude product obtained by heating dibenzyl ketone with hydriodic acid and red phosphorus, appears to be related to dibenzylmethane in the same manner as phenyl-phosphonic or phosphenylic acid, $C^6H^5.PO(OH)_2$, to benzene; when heated with soda-lime, however, it yields scarcely anything but toluene. It is moderately soluble in hot water, sparingly in cold water, easily in alcohol and ether; crystallises in large thick needles, and melts at 142° (Graebe).

DIBENZYL-TETRASULPHONIC ACID, $C^{10}H^{10}(SO^2H)_4$. The potassium salt of this acid, $C^{10}H^{10}(SO^2K)_4 + 3H^2O$, is obtained in small quantity on concentra-

ting the solution of the crude dibenzyl-disulphonate (p. 322), separating at the commencement of the evaporation in small reddish nodules.

DIBROMOBENZENES. See BENZENES (p. 163).

DIUTYL-PHOSPHINE. See PHOSPHINES (2nd Suppl. 955).

DICARBANILIDE, C₆(NH.C^H.CO^H)². See TRICARBANILIDES.

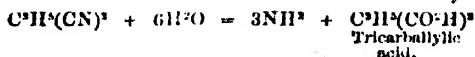
DICHLORALDEHYDE. See ALDEHYDE (p. 53).

DICHLORHYDRIN, C^H₂{ $\begin{smallmatrix} \text{Cl}^2 \\ \text{OH} \end{smallmatrix}$ } On the preparation of this compound, its

oxidation by chromic acid, and its reaction with ammonia, see 2nd Suppl. 317-319. Aniline heated with dichlorhydrin forms dianiline-hydrin, C^H₂(C^H.N)₂O, a compound analogous to diamidohydrin (see p. 635).

When dichlorhydrin is dropped upon phosphoric anhydride, an energetic action takes place, and allylene dichloride is formed by abstraction of water: C^H₂Cl²OH—H²O = C^H₂Cl² (see ALLYLENE, p. 62).

DICHLOROGLYCIDE, C^H₂Cl² = CH²=CCl—CH²Cl. This compound, formed by heating trichlorhydrin with solid potash or soda (ii. 899), boils between 94° and 96°, and has a sp. gr. of 1.21. When heated with an alcoholic solution of pure potassium cyanide, it appears to form in the first instance a mixture of chloro-cyanoglycide, C^H₂< $\begin{smallmatrix} \text{Cl} \\ \text{CN} \end{smallmatrix}$, and dicyanoglycide, C^H₂(CN)₂. The latter, however, immediately takes up the elements of hydrogen cyanide, and is converted into glyceryl tricyanide or tricyanhydrin, C^H₂(CN)₃: for the product when boiled with potash yields a mixture of oxycrotonic acid and tricarballic acid:



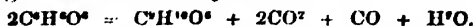
The cyanides cannot be separated, as they decompose when heated; but the acids are non-volatile, and dissolve easily in ether and in alcohol; oxycrotonic acid gives an amorphous soluble lead salt, and tricarballic acid an insoluble lead salt, whereby the two may be separated (A. Claus, *Lichig's Annalen*, clxx. 125).

DICINNHYDROXAMIC ACID, N(C^H²O)²HO. See HYDROXYLAMINE.

DICITRIC ACID. According to Franchimont (*Deut. Chem. Ges. Ber.* vii. 216), the syrupy acid which Hergt obtained by heating citric acid with hydrochloric acid (p. 509), consists of a ditric acid mixed with citric acid. The citric acid obtained from it is said to differ from ordinary citric acid in the character of its crystals.

DICODINE. See CODEINE, under OPIUM-BASES.

DICONIC ACID, C^H²O² (O. Hergt, *J. pr. Chem.* [2], viii. 372). This acid is formed by the action of hydrochloric acid on citric acid at high temperatures. When citric acid is heated with concentrated hydrochloric acid to 140°-150°, it is converted into aconitic acid, together with a syrupy acid possessing the composition and the reactions of citric acid. On heating the mixture to 190°-200°, *diconic acid*, C^H²O², is formed, together with some black resinous matter and the syrupy citric acid, which does not seem to be an isomeride, but common citric acid prevented from crystallising by some admixture: for on heating it again with hydrochloric acid to 140°, it yields aconitic acid, and at 200° it is converted into diconic acid. The latter acid is also obtained by heating aconitic acid with hydrochloric acid:—



Diconic acid is freely soluble in water, alcohol, and ether, and forms small, apparently monoclinic crystals, having a strong acid reaction, and melting at 199°-200°.

Potassium diconate, C^H²O²K², is a very soluble and deliquescent salt. The *ammonium salt*, C^H²O²(NH⁴)², forms a brittle, crystalline, wax-like mass, very soluble and deliquescent. The *barium salt*, 2C^H²O²Ba + 3H²O, is more soluble in cold than in hot water, and is obtained by slow evaporation in hard crystalline crusts, which lose all their water only at 200°. The acid salt, (C^H²O²)²Ba, is an amorphous, glassy, very soluble mass.

The *strontium salt*, C^H²O²Sr + 5H²O, is obtained by slow evaporation as a crystalline frothy mass, which dissolves more freely in cold than in hot water.

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The *calcium salt*, $\text{C}^{\text{H}}\text{O}^{\text{O}}\text{Ca} + \text{H}^2\text{O}$, is a similar body. The *magnesium salt*, $\text{C}^{\text{H}}\text{O}^{\text{O}}\text{Mg} + 6\text{H}^2\text{O}$, forms hard crystalline crusts, dissolving freely in water. When ferric chloride is added to the solution of $\text{C}^{\text{H}}\text{O}^{\text{O}}$ diconate, an orange precipitate is formed, which dries up to an ochre-coloured powder, having probably the composition, $\text{C}^{\text{H}}\text{O}^{\text{O}}\text{Fe}(\text{OH})^2$.

The *manganous salt*, $\text{C}^{\text{H}}\text{O}^{\text{O}}\text{Mn} + 5\text{H}^2\text{O}$, crystallises in colourless probably monoclinic plates. The *cobalt salt*, $\text{C}^{\text{H}}\text{O}^{\text{O}}\text{Co} + 6\text{H}^2\text{O}$, forms small rose-coloured monoclinic plates; the anhydrous salt is blue. The *nickel salt*, $\text{C}^{\text{H}}\text{O}^{\text{O}}\text{Ni} + 6\text{H}^2\text{O}$, crystallises on slow evaporation in pale-green crusts. The *zinc salt*, $\text{C}^{\text{H}}\text{O}^{\text{O}}\text{Zn} + 6\text{H}^2\text{O}$, forms monoclinic plates. The acid salt, $(\text{C}^{\text{H}}\text{O}^{\text{O}})^2\text{Zn} + 7\text{H}^2\text{O}$, seems also to belong to the monoclinic system.

When neutral barium diconate is mixed with lead acetate, small crystals, belonging probably to the quadratic system, separate out. Basic lead acetate produces a flocculent precipitate.

The *copper salt*, $\text{C}^{\text{H}}\text{O}^{\text{O}}\text{Cu} + 3\text{H}^2\text{O}$, is obtained, by slowly evaporating a mixture of moderately dilute solutions of cupric acetate and barium diconate, in hard bluish-green prisms, which are insoluble in water. The *tin salt*, $\text{C}^{\text{H}}\text{O}^{\text{O}}\text{Sn}(\text{SnOH}) + 4\text{H}^2\text{O}$, is a bulky precipitate, which is insoluble in acids.

The *diethylic ether*, $\text{C}^{\text{H}}\text{O}^{\text{O}}(\text{C}^{\text{H}})^2$, is produced by heating the acid gently with absolute alcohol saturated with hydrochloric acid. On adding water to the solution, the ether separates out as a heavy oil which cannot be distilled, and seems to be decomposed by boiling it with water.

Diconic acid is bibasic, but the existence of the basic stannous salt shows that a third hydrogen-atom may also be replaced by a metal. The formula of the acid is therefore $\text{C}^{\text{H}}\text{O}(\text{OH})(\text{CO.OH})^2$.

DICYANODIAMIDE. See CYANAMIDE (p. 599).

DIDYMIUM. A considerable number of didymium salts prepared and analysed by Cleve in 1874, have been described in the article *CERITE-METALS* (p. 424); quite recently, however, a further investigation of the compounds of this metal has been made by Frerichs a. Smith (*Liebig's Annalen*, 1878, exlix. 331), who have described a new method of separating didymium and lanthanum, and prepared several salts of these metals not previously examined.

1. *Separation of Didymium and Lanthanum from Cerium.*—The mixture of oxides and carbonates of the three metals obtained by decomposing pulverised cerite with sulphuric acid, lixiviating the sulphates with cold water, precipitating with oxalic acid, and igniting the dried precipitate, is repeatedly moistened with nitric acid, and again ignited, whereby a mixture is obtained, consisting chiefly of lanthanum oxide, didymium oxide, and ceric oxide. To remove the latter, the crude oxides are drenched in a basin with a large quantity of water (about 5 litres to 500 grams of oxide), and the liquid is boiled for several days, while very dilute nitric acid is allowed to flow slowly into it from a dropping pipette, so as to keep it slightly acid. This very dilute acid does not attack the oxides of cerium, but readily dissolves those of lanthanum and didymium. The filtered solution, which is quite free from cerium, is mixed with sulphuric acid, concentrated by evaporation, treated with hydrogen sulphide to free it from small quantities of metals precipitable thereby, and the filtrate is mixed with a hot solution of potassium sulphate, which throws down the lanthanum and didymium as double sulphates, leaving the gadolinite metals and others in solution. By decomposing the precipitated didymio-potassic and lanthano-potassic sulphates with sodium carbonate, dissolving the precipitated carbonates in nitric acid, treating the solution with oxalic acid, and igniting the precipitated oxalates, a preparation is obtained consisting wholly of the oxides of didymium and lanthanum.

2. *Separation of Lanthanum and Didymium.*—Frerichs a. Smith obtain a didymium salt free from lanthanum, and a lanthanum salt free from didymium:

a. By Erk's method of partial precipitation with ammonia (*2nd Suppl.* 428).

β. By mixing the solution of the nitrates of the two metals with a quantity of sulphuric acid sufficient to convert only a part of the lanthanum (the stronger base) into sulphate—so that after four or five days the solution consists of a mixture of lanthanum sulphate with the nitrates of lanthanum and didymium—and mixing the solution with alcohol, which throws down nearly all the lanthanum sulphate, leaving the two nitrates still dissolved. After crystallising the precipitated sulphate a few times from water, a salt was obtained in which not a trace of didymium could be detected by the spectroscope. By this process, therefore, a salt of lanthanum was obtained free from didymium.

The alcoholic solution filtered from the lanthanum sulphate contained didymium nitrate, together with a small quantity of lanthanum nitrate. To obtain from it a pure didymium salt, the alcohol was distilled off; the remaining solution, after dilution

with water, was mixed with a quantity of sulphuric acid, sufficient to convert part of the didymium as well as the whole of the lanthanum, into sulphate; and after four or five days, the greater part of these sulphates was precipitated by alcohol. The solution was then evaporated down; and the dry mixture of didymium nitrate and a small quantity of didymium and lanthanum sulphates (these sulphates being somewhat soluble in dilute alcohol) was heated in a platinum crucible nearly to redness, whereby the nitrate was decomposed, while the sulphates remained unaltered. The finely pounded mass was then treated with cold water to extract the sulphates, and the undissolved residue of didymium oxide was washed with water, till neither the washings nor the solution of the didymium oxide in nitric acid showed any turbidity with barium chloride, a process which had to be continued for about a week. The didymium oxide was then converted into sulphate, this salt was dissolved in seven times its weight of cold water, and the solution was slowly warmed in a platinum dish. Crystallisation began at 86° , the solution yielding large well-defined rose-coloured crystals which were taken out from time to time.

As no characteristic reaction of lanthanum is known, the purity of the didymium salt was tested by analysing the first and last crystals which separated out; and as both analyses yielded the same result—whereas lanthanum sulphate, if present, would have crystallised out first, and would therefore have made a difference in the composition of the first crop of crystals—the didymium sulphate was judged to be pure. This conclusion was strengthened by the fact that the salt began to crystallise only at 86° , whereas lanthanum sulphate crystallises out almost completely at 60° .

The atomic weight of (trivalent) didymium thus purified was found to be 144.

The following are the compounds of didymium analysed by Frerichs & Smith.

Platinochloride, $2\text{DiCl}^3 \cdot 3\text{PtCl}^4 + 24\text{H}^2\text{O}$.—Obtained by mixing concentrated solutions of didymium chloride and platonic chloride. Very fine orange-coloured tables.

Aurochloride, $2\text{DiCl}^3 \cdot 3\text{AuCl}^3 \cdot 21\text{H}^2\text{O}$.—Brilliant yellow plates, very hygroscopic and deliquescent.

Oxychloride, DiOCl .—Obtained by heating didymium oxide in chlorine. Resolved by boiling with water into hydrate and chloride.

Didymium and Zinc Bromide, $2\text{DiBr}^3 \cdot 3\text{ZnBr}^2 \cdot 36\text{H}^2\text{O}$.—Reddish-brown needles, very hygroscopic, taking up water even from calcium chloride.

Didymium and Nickel Bromide, $2\text{DiBr}^3 \cdot 3\text{NiBr}^2 \cdot 18\text{H}^2\text{O}$.—Small brownish crystals, which rapidly absorb water from the air.

Didymium and Zinc Iodide, $2\text{DiI}^3 \cdot 3\text{ZnI}^2 \cdot 24\text{H}^2\text{O}$.—Small yellowish needles, very hygroscopic.

Fluoride, $2\text{DiF}^3 \cdot (\text{HF})^3$.—Thrown down as a gelatinous precipitate on adding hydrofluoric acid to a solution of didymium sulphate. Over the water-bath it dries up to a transparent rose-coloured mass.

Peroxide, $\text{Di}^4\text{O}^2 \cdot \dagger$.—An oxide having this composition was obtained as a chestnut-brown powder by decomposing the nitrate at a gentle heat, and then heating the residual oxide to low redness in a current of oxygen. It dissolves in nitric acid, giving off oxygen.

Sulphide, Di^4S^2 .—A yellow or brownish substance obtained by heating the oxide in vapour of carbon bisulphide. It dissolves easily in acids, giving off hydrogen sulphide.

Nitrate, $\text{DiO}^2(\text{NO}^3)^3 \cdot 6\text{H}^2\text{O}$.—Large violet crystals having this composition are obtained by dissolving the oxide in nitric acid and evaporating the solution over sulphuric acid. The salt absorbs water from the air, becomes anhydrous at 200° , and melts without decomposition at 300° . It dissolves easily in alcohol. Forms crystalline compounds with other nitrates.

Didymium and Zinc Nitrate, $2\text{DiO}^2(\text{NO}^3)^3 \cdot 3\text{ZnO}^2(\text{NO}^3)^2 \cdot 69\text{H}^2\text{O}$.—Deliquesces extremely rapidly in the air.

Didymium and Nickel Nitrate, $2\text{DiO}^2(\text{NO}^3)^3 \cdot 3\text{NiO}^2(\text{NO}^3)^2 \cdot 36\text{H}^2\text{O}$.—Large bright-green tables, hygroscopic and very easily soluble in water.

Didymium and Cobalt Nitrate, $2\text{DiO}^2(\text{NO}^3)^3 \cdot 3\text{CoO}^2(\text{NO}^3)^2 \cdot 48\text{H}^2\text{O}$.—Dark-red crystals, obtained with great difficulty. Very soluble.

Hypochlorite, $\text{Di}(\text{OCl})^3$.—Obtained by passing chlorine into water in which didymium hydroxide is suspended. Thin nearly colourless tables, dissolving sparingly in water, but easily in strong acids.

Basic Sulphate, $[\text{Di}(\text{OH})^3]^2 \cdot (\text{SO}^4)^2$.—Ammonia added to the neutral sulphate

* Respecting the platinochloride, aurochloride, fluoride, selenate, and pyrophosphate, compare Cleve, p. 424.

† Di^4O^2 , according to Hermann, for univalent didymium, $[\text{Di}^4=48]$. See II. 321.

throws down a gelatinous precipitate which dries up to a mass having this composition. The salt is insoluble in water, but easily soluble in acids.

Neutral Sulphate, $\text{Di}^2(\text{SO}_4)^2$.—This salt crystallises from strongly acid solutions in rose-red crystals containing $6\text{H}_2\text{O}$, and from neutral saturated solutions on slow evaporation in crystals containing $9\text{H}_2\text{O}$. The latter give off two-thirds of their water at 200° .

Selenate, $\text{Di}^2(\text{SeO}_4)^2 \cdot 6\text{H}_2\text{O}$.—Fine rose-red prisms, very easily soluble in water, obtained by evaporating a solution of the oxide in selenic acid.

Selenite, $\text{Di}^2(\text{SeO}_3)^2 \cdot 6\text{H}_2\text{O}$.—Obtained as a gelatinous precipitate on adding alcohol to a mixture of concentrated solution of didymium nitrate with selenious acid.

Phosphate, $\text{DiPO}_4 \cdot \text{H}_2\text{O}$.—Obtained by boiling solutions of didymium with phosphoric acid, or by adding trisodium phosphate to didymium sulphate. Insoluble in water; soluble in acids.

Triphosphate, $\text{Di}^2(\text{HO}^3\text{PO})^3$.—Precipitated from the sulphate by disodium phosphate.

Pyrophosphate, $\text{Di}^2(\text{H}^2\text{O}^2\text{P}^2\text{O})^2$.—Precipitated by neutral sodium pyrophosphate from acid solutions of didymium. Soluble in excess of the precipitant.

Metaphosphate, $\text{DiO}^2(\text{PO}^2)^2$.—Rose-red powder, precipitated by sodium metaphosphate from didymium sulphate.

Arsenate, $\text{Di}^2(\text{HO}^3\text{AsO})^3$.—Pale-red precipitate thrown down by disodium arsenate from didymium sulphate. Insoluble in water.

Phosphite, $\text{Di}^2(\text{O}^2\text{PHO})^2$.—Precipitated from solutions of didymium by disodium phosphite.

Arsenite, $\text{Di}(\text{O}^2\text{AsHO})^2$.—A white granular powder, insoluble in water, formed by boiling didymium hydrate with aqueous solution of arsenious acid.

Chromate, $\text{Di}^2(\text{O}^2\text{CrO}^2)^2$.—A yellow granular powder, precipitated by potassium dichromate from didymium sulphate. Dissolves sparingly in water, easily in dilute acids.

Manganate, $\text{Di}^2(\text{O}^2\text{MnO}^2)^2$.—Formed by heating didymium nitrate with manganese dioxide. Black powder, insoluble in water, soluble with dark-red colour in sulphuric acid.

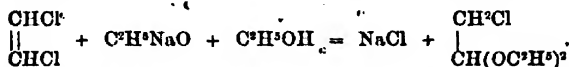
Permanganate, $\text{Di}(\text{MnO}_4)^2 \cdot 21\text{H}_2\text{O}$.—Deposited from a mixture of potassium permanganate and didymium sulphate on standing. Reddish-brown crystalline powder, sparingly soluble in water.

Borate, $\text{Di}^2(\text{O}^2\text{B}^2\text{O})^2$.—Thrown down as a white gelatinous precipitate on adding sodium borate to a solution of didymium sulphate. Insoluble in water.

Molybdate, $\text{EiH}^2\text{O}^4(\text{MoO}_2)^2$.—Obtained as a pale-red gelatinous precipitate by adding ammonium molybdate to solutions of didymium.

Tungstate, $\text{Di}^2(\text{O}^2\text{WO}_2)^2$.—Precipitated by disodium tungstate from didymium sulphate. Gelatinous precipitate, drying up to a rose-red mass, insoluble in water.

DIETHOXYLETHANE (CHLORO-), $\text{C}^2\text{H}^2\text{Cl}(\text{OC}^2\text{H}^2)^2$. This compound is formed by the action of alcoholic sodium ethylate on dichlorethylene at high temperatures:



Chlorodiethoxyethane is a colourless oily liquid having a peculiar aromatic odour, a density of 1.026 at 15° , and boiling at 155° (Klien, *Jenaische Zeitschr. f. Naturw.* x. 67).

DIETHYLACETIC or ISOCAPROIC ACID. See CAPROIC ACIDS (p. 378).

DIETHYL-ACETO-ACETIC ETHER,

$\text{C}^{10}\text{H}^{18}\text{O}^2 = \text{CH}^3\text{CO} \cdot \text{O} \cdot \text{C}(\text{CH}^3)^2 \cdot \text{COOC}^2\text{H}^5$. See ACETO-ACETIC ETHERS (p. 13).

DIETHYLALLYLAMINE, $\text{C}^7\text{H}^{15}\text{N} = (\text{C}^2\text{H}^5)_2\text{C}(\text{C}^3\text{H}^5)\text{N}$. See ALLYLAMINES (p. 62).

DIETHYLANILINE-SULPHONIC ACID, $\text{C}^8\text{H}^7[\text{N}(\text{C}^2\text{H}^5)^2]\text{SO}^3\text{H}$. See BENZENESULPHONIC ACIDS (AMID-), (p. 235).

DIETHYL-BORIC ACID or *Boric Diethohydrate*, $(\text{C}^2\text{H}^5)^2\text{B}(\text{OH})$. See BORON. ORGANIC COMPOUNDS OF (p. 348).

DIETHYL-CARBAMIDE. v. Zotta, by passing nitrous acid into an alcoholic solution of symmetrical diethylcarbamide, $\text{NH}(\text{C}^2\text{H}^5)_2 \cdot \text{CO} \cdot \text{NH}(\text{C}^2\text{H}^5)_2$, obtained an oily liquid, to which he assigned the formula $\text{C}^2\text{H}^5-\text{N} < \begin{array}{c} \text{N}(\text{OH}) \\ \text{CO} \end{array} > \text{N}-\text{C}^2\text{H}^5$ (p. 390). E.

Fischer, however, finds that this compound is nitrosodiethylcarbamide, $\text{NH}(\text{C}^2\text{H}^5)\cdot\text{CO}\cdot\text{N}(\text{NO})(\text{C}^2\text{H}^5)$. The easiest way of preparing it is to pass nitrous acid in excess into a solution of diethylcarbamide in ether. On leaving the ether to evaporate at a very low temperature, washing the residual oil with water, drying it over calcium chloride, again evaporating, and leaving the oily residue for a considerable time at a

alcoholic solution with zinc-dust and acetic acid, it is reduced to diethyl-hydrazine-carbamide (*Deut. Chem. Ges. Ber.* ix. 111).

DIETHYL-CARBINOL. See ALKYL ALCOHOLS (p. 77).

DIETHYL-DIETHYLAMMONIUM COMPOUNDS. See METHYLAMINES.

CARBAMIDE, $\text{C}(\text{C}^2\text{H}^5)_2(\text{C}^2\text{H}^5)_2\text{N}^2\text{O}$ (p. 391).

See PHENYLAMINES.

DIETHYL-FLUORESCIN. See FLUORESCIN.

DIETHYL-GLYCINE or **DIETHYL-GLYCOCINE.** See GLYCINE.

See HYDRAZINE-COMPOUNDS.

ETHER, $\text{C}^2\text{H}^5(\text{C}^2\text{H}^5)_2\text{O}\cdot\text{C}^2\text{H}^5$. See ETHYL OXIDE.

DIETHYLIDENE-AMMONIUM THIOCARBAMATE. See CARBOTHALDINE (p. 387).

DIETHYLIDENE-LACTAMIC ACID, $\text{C}^2\text{H}^4\text{NO}^2$, also called *Didenlactamic acid* and *Dilactamic acid* (2nd Suppl. 722). This acid, like other amliated acids, affords both with bases and with acids. The following compounds are described by Heintz (*Liebig's Annalen*, clxv. 44).

The *acid ammonium salt*, $\text{C}^2\text{H}^4(\text{NH}^+)\text{NO}^2$, obtained by adding excess of ammonia to diethylidene-lactamic acid, and evaporating to a syrup on the water-bath, crystallises on cooling in needles which may be recrystallised from alcohol. The salt separates from this solvent in rectangular tables, but when it is deposited from a mixture of alcohol and ether, it often takes the form of needles. It is very soluble in water, slightly soluble in alcohol, and insoluble in ether, decomposes at a temperature below its melting point, and on distillation yields ammonia and a thick liquid, partly soluble in water.—The *barium salt* is obtained by neutralising didenlactamic acid with excess of barium hydrate, removing the superfluous base by means of carbonic anhydride, and evaporating the slightly alkaline liquid. The syrupy residue which remains gradually dries up to a brittle fissured mass. If alcohol be added to an aqueous solution of this salt, the latter is separated in a syrupy form. The action of acetic acid on it did not give rise to the formation of a crystalline acid salt.—The *zinc salt*, $\text{C}^2\text{H}^4\text{ZnNO}^2$, obtained by boiling diethylidene-lactamic acid with basic zinc carbonate and a considerable quantity of water, filtering hot, and evaporating, consists of microscopical quadratic tables, very slightly soluble in water, but easily soluble in hydrochloric acid.—The *cadmium salt*, $\text{C}^2\text{H}^4\text{CdNO}^2$, is prepared by boiling a dilute aqueous solution of the acid with cadmium carbonate, evaporating the solution, treating the residue several times with hot water, and pressing the undissolved portion, and may be obtained in microscopic needles by boiling its cold saturated solution. It is very soluble in cold water, although it dissolves but slowly. The solution, on evaporation over sulphuric acid, yields a syrupy residue, which gradually becomes opaque and partially solid. While the syrup remains transparent, it dissolves readily in cold water, but when it has become solid and opaque, it is no longer easily soluble; the change into the less soluble variety appears to be accompanied by partial dehydration. On boiling a cold saturated solution, the partially dehydrated salt is deposited in needles having the composition $\text{C}^2\text{H}^4\text{CdNO}^2 + \text{H}^2\text{O}$. The salt dried at 160° contains $\text{C}^2\text{H}^4\text{CdNO}^2$.—*Lead salt*, $\text{C}^2\text{H}^4\text{PbNO}^2$. An aqueous solution of diethylidene-lactamic acid saturated with lead hydrate forms a strongly alkaline liquid, from which almost all the excess of lead may be removed by means of carbonic anhydride. On filtering this solution, slightly acidulating with acetic acid, evaporating, and adding alcohol, the lead salt separates in crystalline crusts; when crystallised from dilute alcohol it has a slightly alkaline reaction.—The *silver salt*, $\text{C}^2\text{H}^4\text{Ag}^+\text{NO}^2$, is obtained as a white precipitate when a soluble salt of the acid is precipitated by silver nitrate. Like silver diglycollamate, it explodes slightly when heated. From boiling water it separates partly in small rhombic tables, partly in needles, which are sometimes united in tufts.

Hydrochloride, $2\text{C}^2\text{H}^4\text{NO}^2\cdot\text{HCl}$.—When diethylidene-lactamic acid is dissolved in

fuming hydrochloric acid, and the solution is evaporated in a vacuum, a syrupy mass is obtained which dissolves in a small quantity of absolute alcohol, and is separated from it in the fluid state on addition of water. If the previously mentioned solution be evaporated, and the residue be dissolved in a small quantity of water, it yields on evaporation over sulphuric acid, a syrupy mass, in which flat microscopic needles gradually form. If, however, the residue be dissolved in absolute alcohol and ether be added, small crystals are deposited, which consist of a compound soluble in alcohol or ether and permanent in the air. This substance dissolves in water, and the solution on spontaneous evaporation yields colourless rhombic prisms.

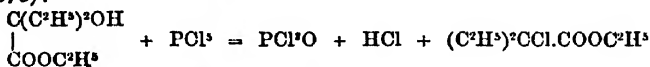
Nitrate.—Diethylidenelactamic acid dissolves readily in nitric acid, and the solution, when evaporated over sodium hydrate, gives a thick syrup, which, when dissolved in warm alcohol and separated by the cautious addition of ether, takes the form of fringed hemispherical grains, apparently made up of groups of thin concentric needles.

Nitrosodiethylidenelactamic acid, $C^6H^{10}(NO)NO^2$.—The calcium salt of this acid is obtained by gradually adding calcium nitrite to a solution of diethylidenelactamic acid in nitric acid, the solution being stirred to prevent local heating. Sufficient calcium nitrite having been added to make the liquid permanently green, it is diluted, gently warmed, neutralised with lime, and evaporated almost to dryness, the residue dissolved in alcohol, and the solution mixed with ether, which throws down the calcium salt of the nitroso-acid. The free acid may be obtained from this salt either by decomposing it with the requisite quantity of oxalic acid, or by precipitating it with ammonia and ammonium carbonate, boiling the ammonium salt thus obtained with barium hydrate, and decomposing the barium salt with the requisite quantity of sulphuric acid. It forms a syrup which finally solidifies to small colourless flat needles, consisting partly of elongated rhombic tables and partly of elongated six-sided tables. It is easily soluble in water or alcohol, and is dissolved by ether. With concentrated sulphuric acid and ferrous sulphate it gives the well-known reaction of the higher oxides of nitrogen.

DIETHYL-METHYL-ACETIC ACID, $C(C^2H^3)^2CH^3-COOH$. See HETEROIC ACIDS.

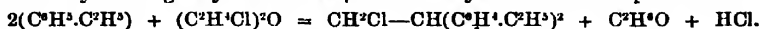
DIETHYL-METHYLAMINE METHIODIDE. See METHYLAMINES.

DIETHYLOXALATE or **DIETHOXALATE**, **ETHYLIC**. This ether, treated with phosphorus pentachloride, yields the ethylic ether of chlorisocaproic acid (p. 378):



DIETHYLOXAMIDE. See OXAMIDE.

DIETHYL-PHENYL-MONOCHLOROETHANE, $CH^3Cl-CH(C^6H^4.C^2H^3)^2$, is formed by treating ethyl-benzene with dichlorethyl chloride and sulphuric acid:



When subjected to distillation, it is resolved into hydrochloric acid and diethylstilbene, $C^{14}H^{11}Cl(C^2H^3)^2 = HCl + C^{14}H^{10}(C^2H^3)^2$ (Klepp, *Deut. Chem. Ges. Ber.* vii. 1414).

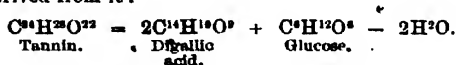
DIETHYL-PHENYL-PHOSPHINE, $P(C^2H^3)^2(C^6H^5)$. See PHOSPHINES.

DIETHYL-STILBENE. See STILBENE under DIPHENYL-COMPOUNDS.

-URBA. See CARBAMIDES (p. 390).

See GASES and LIQUIDS.

DIGALLIC ACID, $C^{14}H^{10}O^3 = 2C^7H^5O^3$ (gallic acid) $- H^2O$. This, according to Schiff's latest researches (*Liebig's Annalen*, clxx. 43; *Gazz. chim. ital.* 1873, 553), is the composition of pure gallotannic acid, natural tannin from nutgalls being probably a glucoside derived from it:



See further, Paul a. Kingzett (*Chem. Soc. J.* 1878, xxxiii. 217); also the article TANNIN in this volume.

*Digallic acid is not formed by the action of sulphuric acid on gallic acid. The formation of rufgallic acid from digallic acid by the action of sulphuric acid is rather preceded by the formation of gallic acid and a brown substance which contaminates the rufgallic acid thus produced (see 2nd Suppl. p. 1143).

DIGESTION. Observations on digestion through the agency of a gastric fistula have been made by C. Richet (*Compt. rend.* lxxxiv. 450; *Chem. Soc. J.* 1877, ii. 631). On the Differences of Digestion and of Chemical Structure amongst Animals, see Hoppe-Seyler (*Pflüger's Archiv. für Physiologie*, xiv. 395; *Chem. Soc. J.* 1877, ii. 395).

On the Resorption and Sécretion of Alimentary Constituents in the Digestive Canal of the Sheep, see E. Wildt (*Chem. Centr.* 1875, 40, 57, 72; *Jahresb. f. Chem.* 1875, 864).

On the Digestion of Fats: H. C. Bartlett (*Analyst*, 1877, 175; *Chem. Soc. J.* 1877, ii. 207).

On the Digestion of Linseed Mucilage with Artificial Gastric Juice: Fudakowski, (*Chem. Centr.* 1877, 6; *Chem. Soc. J.* 1877, ii. 911).

On the Digestibility of Fodder: Pott a. Pfeiffer (*Journal für Landwirtschaft*, xxii. 370; *Jahresb. f. Chem.* 1874, 924).

Pancreatic Digestion.—According to Radziszewski and E. Salkowski (*Deut. Chem. Ges. Ber.* vii. 1050), aspartic acid is found amongst the products of the pancreatic digestion of blood-fibrin. Nencki (*ibid.* 8593) obtained from the products of the pancreatic digestion of fibrin, a distillate exhibiting all the reactions of indol. By the pancreatic digestion of gelatin, Nencki obtained very little indol, small quantities of tyrosine, ammonia, leucine, and glycocine, and a viscid yellowish body which he designates as gelatin-peptone.

On the Separation of Digestive Ferments, see FERMENTS.

DIGITALIS. The active principles of fox-glove (*Digitalis purpurea*) have lately been made the subject of numerous investigations, but the results are not very satisfactory, and those obtained by different experimenters are in many respects discordant.

Nativelle (*Pharm. J. Trans.* [3], ii. 865 [1872]) obtains crystallised digitalin by exhausting the leaves with alcohol and mixing the concentrated solution diluted with three times its bulk of water, whereby a precipitate is obtained consisting of digitalin and digitin, the former easily soluble in chloroform, the latter insoluble (1st Suppl. 346). Digitalin thus obtained crystallises in slender shining needles grouped around a common axis, and exhibiting conspicuously the characteristic emerald-green colour on treatment with hydrochloric acid (ii. 329).

The amorphous substance obtained from the aqueous extract of fox-glove leaves and sometimes called digitalin, is designated by Nativelle as digitalein (*comp. Kosmann*, ii. 328). It exhibits the characteristic green coloration in a minor degree, and its physiological action is less marked than that of crystallised digitalin.

More recently, 1875 (*J. Pharm. Chin.* [4], xx. 81; *Chem. Soc. J.* xxviii. 276), Nativelle has described a method of preparing crystallised digitalin differing but little from that which he gave in 1869 (1st Suppl. 645).

According to Flückiger (*N. Jahrb. Pharm.* xxxix. 129; *Chem. Centr.* 1873, 371; *Jahresb. f. Chem.* 1873, 814), crystallised digitalin forms small microscopic plates, which lose 6·8 per cent. of their weight by standing over sulphuric acid. It is very soluble in chloroform, much less in ether. Its most characteristic reaction is the fine green colour which it assumes when added to a small quantity of phosphoric acid concentrated as much as possible on a watch-glass, the acid at the same time becoming yellow.

N. Goerz (*Russ. Zeitschr. Pharm.* 1873, 385 and 417; *Jahresb. f. Chem.* 1873, 816), following the directions given by Nativelle (1872), has also obtained digitalin (crystalline), digitin, and digitalein, but in much smaller quantities (possibly the leaves on which he worked were less rich in active principles than the French fox-glove leaves treated by Nativelle); moreover, the crystallised digitalin was physiologically inactive.

Digitin crystallises, according to Goerz, in stellate groups of needles soluble in hot alcohol and separating out on cooling. Chloroform and benzene dissolve only traces of it, but ether dissolves half its weight of digitin, which however remains in the amorphous state on evaporating the solvent. It is insoluble in water, but soluble in alkalis, and is precipitated therefrom by acids. Strong sulphuric acid dissolves digitin, forming a brown-yellow solution, which, when exposed to the air, gradually acquires a purple-red colour extending from the edges inwards: the addition of water turns it green. Digitin is insoluble in hydrochloric acid, but dissolves without coloration in nitric acid. When heated it first melts without decomposing, then turns brown, swells up, and burns, giving off greyish-white vapours having a resinous odour. It does not reduce Fehling's solution, but after treatment with sulphuric acid it exhibits a strong reaction of sugar, whence it appears to be a glucoside. It is free from nitrogen, and, from the results of three elementary analyses, appears to have a composition represented by the empirical formula $C^4H^6O^2$.

Digitalein is obtained as a fine light yellow powder having a pleasant odour of digitalis and a very bitter taste; when brought in contact with the mucous membranes of the nose it produces violent sneezing. It dissolves easily in water and in alcohol, but is nearly insoluble in ether, chloroform, and benzene. Sulphuric acid dissolves digitalein with a dingy green colour, but, on adding a drop of hydrochloric acid, three coloured rings are produced, the outer being emerald-green, the middle orange-yellow, and the inner orange-red; afterwards the solution acquires a uniform emerald-green colour. Potassium bromide and sulphuric acid produce a rose-red colour gradually changing to purple-red, and becoming green on addition of a small quantity of hydrochloric acid. The aqueous solution of digitalein forms with platonic chloride a light yellow flocculent precipitate, and with silver nitrate a white gelatinous precipitate; no precipitate with mercuric chloride, cupric sulphate, or tincture of iodine.

Digitalein is a non-azotised glucoside, and the analyses of Goerz (which, however, do not appear to be very exact,) lead to the empirical formula $C^{12}H^{20}O^4$. Goerz is inclined to regard digitalein as identical with the digitalin (or digitalein) of Walz (ii. 329). At all events its physiological action shows that it possesses all the active properties observed in digitalis, and that in a therapeutic point of view it is a very important substance. Goerz regards the discovery of a simple method of preparing digitalein as the most important result of Nativelle's researches.

On Digitalin and the other proximate principles of Fox-glove, see also Kosmann (*J. Pharm. Chim.* [4], xx. 427; *Chem. Soc. J.* 1875, 650), and Schmiedeberg (*Pharm. J. Trans.* [3], v. 741; *Chem. Soc. J.* 1875, 1266).

Detection of Digitalin.—This substance may be detected by the red colour produced when its solution is mixed with a dilute aqueous solution of dried ox-bile, and then with a quantity of sulphuric acid sufficient to raise the temperature to 70° . This reaction is sufficiently delicate to detect the presence of digitalin in a decoction of 0.3 gram of fox-glove leaves in 180 grams of water: it likewise serves to distinguish digitalin from all alkaloids excepting those which directly give a red colour with sulphuric acid. The acid ethereal extracts to be dealt with in toxicological investigations may also contain lactic acid, tartaric acid, colchicine, atropine, and picro, but none of these substances give the bile-reaction above described (H. Brunner, *Chem. Ges. Ber.* 1873, 96).

According to Almqvist, on the other hand (*Arch. Pharm.* [3], v. 515), sugar, glucosides, starch, dextrin, inulin, and cellulose, also give the red colour with bile and sulphuric acid, and consequently, as these substances often occur in extracts and decoctions, Brunner's test for digitalin is applicable only when that substance has been obtained in the separate state.

On the detection of Digitalin in Mixtures of Alkaloids and other proximate principles of vegetables, see PLANT-BASES.

DIGITIN. See the last article.

DIGLYCOLLAMIC DIURAMIDE, $C^8H^{11}N^2O^4 = NH(NH^2.CO.NH.CO.CH^2)^2$. This compound is formed by heating bromacetyl-urea with alcoholic ammonia to 100° in a sealed tube, or by passing dry ammonia gas through alcohol at 70° – 80° , containing bromacetyl-urea. It melts at 195° – 200° , dissolves sparingly in cold, somewhat readily in warm water, and crystallises in slender needles.

The crude product of the above reaction, heated with dilute hydrochloric acid and recrystallised from water, yielded a compound apparently consisting of triglycollamic triuramide, $N(NH^2.CO.NH.CO.CH^2)^3$ (E. Mulder, *Dent. Chem. Ges. Ber.* v. 1011).

DIGLYCOLLIC ACID, $C^8H^8O^4$. Several salts of this acid have been examined by G. Schreiber (*J. pr. Chem.* [2], xiii. 436). The lithium salt, $C^8H^8O^4Li^2 + 5H^2O$, crystallises from a moderately concentrated solution in small colourless transparent crystals, and from a syrupy solution in concentric groups of small nodules, exhibiting under the microscope the appearance of prismatic laminae. It dissolves in 2.2 pts. of water at 18.6° . It is soluble also in dilute, but insoluble in absolute alcohol, which precipitates it from a strong aqueous solution in crystalline nodules containing $2\frac{1}{2}$ mols. H^2O . An acid barium salt, $C^8H^8O^4Ba$, was once obtained in small hard, granular, transparent crystals. The strontium salt, $C^8H^8O^4Sr + 4H^2O$, was obtained in small limpid, non-efflorescent crystals containing 4 mols. H^2O , which were given off completely at 240° .

DIDYDRACTYLIC ACID, $C^8H^{10}O^4 = (C^2H^4.OH)^2O$. See 2nd Suppl. 721; also p. 47 of this volume.

DIDYDROPLUMIERIC ACID. See PLUMIERIC ACID.

ZOIC ACID, $C^8H^7(NH^2)COOH$. See BENZOIC ACID

DERIVATIVES, p. 271.

DI-IODAZOBENZOIDIC ACID, $C^{14}H^8I^2N^2O^4$ (p. 274).

DI-IODHYDRIN, $C^8H^{10}(OH)I^2$, may be prepared by heating dichlorhydrin with potassium iodide and water in a salt-bath. The product separated from free iodine by agitation with very weak sulphuretted hydrogen water, is a faintly yellow viscid oil, having a density of 2.4, solidifying at -16° to -20° to a white crystalline mass, and decomposing when distilled (Nahmacher, *Deut. Chem. Ges. Ber.* v. 353).

DI-ISETHIONAMIC ACID, $NH(CH^2CH^2SO^2OH)^2$. This appears to be the constitution of an acid formed by the action of baryta-water on taurine. Its acid ammonium salt, which is isomeric with taurine, forms a light powder having a silky lustre, and made up of crystalline scales. The barium salt crystallises with remarkable facility (E. Salkowski, *Deut. Chem. Ges. Ber.* vii. 116).

DI-ISOBUTYLENE, $C^8H^{16} = (CH^3)^2C = CH^2 - CH^2 = C(CH^3)^2$. This hydrocar-

bon is the chief product obtained when isobutylene is heated to 100° with a mixture of equal parts of strong sulphuric acid and water (with very weak acid the chief product is trimethyl carbinol). It unites directly with hydrobromic and hydriodic acids, and the hydroxide, treated with moist silver oxide, is converted into an octyl alcohol, $C^8H^{18}O$, which solidifies at -20° to a white crystalline mass, and retains water with great obstinacy. Di-isobutylene and the octyl alcohol derived from it are converted by oxidising agents, e.g. chromic and metaphosphoric acids, into acetone and trimethylacetic acid, together with carbon dioxide, acetic acid, an octoic acid, $C^8H^{16}O^2$, and a ketonic substance, $C^7H^{14}O$. Hence, the structure of di-isobutylene may probably be represented by the formula $(CH^3)^2C = CH - C \equiv (CH^3)^2$ (Butlerow, *Deut. Chem. Ges. Ber.* viii. 1683, ix. 1687; *Liebig's Annalen*, clxxx. 245).

DI-ISOPROPYL KETONE, $CO[CH(CH^3)^2]^2$. See PROPYL KETONES.

TELL-OIL. Gladstone found in this oil a terpene boiling at 173° , and strongly dehydratory (ii. 188). Nietzki (*Arch. Pharm.* [3], iv. 317-324) finds in addition a resinous substance boiling above 230° , and an oxidised body which, after purification by combination with sulphuretted hydrogen, washing the crystalline product with alcohol, pressing, and decomposition by caustic potash solution, boils at 223° - 229° , and appears to be identical with carvol. Moreover, the terpene present does not appear to be homogeneous, as it does not distil at a constant temperature, one portion boiling at 155° - 160° , and another at 175° . Neither specimen appeared to be absolutely free from oxidised substances, even after many rectifications over sodium: the higher-boiling terpene resembled oil of mace in odour, the lower one was turpentine-like (probably terebene).

The higher terpene, after standing for some months in contact with nitric acid, alcohol, and water, gave crystals melting at 103° , and having the composition of terpene hydrate, $C^{10}H^{16}.3H^2O$ or $C^{10}H^{20}O^2.H^2O$. With hydrochloric acid gas it gave an oily hydrochloride, $C^8H^{16}.HCl$, and by heating for twelve hours with half its weight of iodine in a flask with inverted condenser it produced cymene and hydriodic acid. This cymene boiled between 175° - 180° , and yielded on oxidation by nitric acid a substance melting at 176° , and having the properties of paratoluic acid; with dichromate of potassium and sulphuric acid, substances recognised qualitatively as terephthalic and acetic acids were formed.

DIMESITYLENE-SULPHAMIDE, $(C^8H^{11}SO^2)^2NH$. See MESITYLENE-COMPOUNDS.

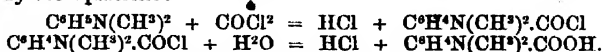
DIMETATOLYL-THIOCARBAMIDE, $CSN^2H^2(C^8H^4.CH^3)^2$. See TOLYL-COMPOUNDS.

DIMETHOXYPHENYLMETHANE, $C^{16}H^{16}O^2 = CH^2(C^6H^4-O-CH^3)^2$ (E. ter Meer, *Deut. Chem. Ges. Ber.* vii. 1200). This compound is formed on adding a cooled mixture of 26 grms. anisol and 280 grms. glacial acetic acid, to a mixture of 60 grms. anisol, 15 methylal, and 280 glacial acetic acid, the liquid becoming slightly warm, and acquiring first a faint reddish-violet, and then a blue-violet colour. The mixture, after standing for twenty-four hours, is neutralised with soda-ley and exhausted with ether, and the ethereal solution is subjected to fractional distillation, the portion passing over above 360° being collected apart. This distillate, which solidifies on cooling, is dissolved in alcohol, and the well-cooled solution is made to crystallise by dropping into it a ready-formed crystal of the compound.

Dimethoxyphenylmethane crystallises in small white rhombic laminae having a fatty lustre. It melts at 52° and boils at a temperature above the boiling point of mercury. It dissolves in all proportions in hot alcohol, easily in cold alcohol, in glacial acetic acid, ether, and benzene, but is insoluble in water. It easily forms supersaturated solutions. It dissolves in sulphuric acid, especially if gently heated,

with a fine red colour, and is not precipitated from the solution by water. Fuming nitric acid acts strongly on it, forming nitro-products.

DIMETHYLAMIDOBENZOIC ACID, $\text{C}^6\text{H}^4\text{N}(\text{CH}_3)_2\text{COOH}$ (W. Michler, *Deut. Chem. Ges. Ber.* ix. 400). The chloride corresponding with an acid of this composition, is obtained by the action of carbonyl chloride on dimethylaniline at ordinary temperatures, or more readily at 50° in a sealed tube. The product is a blue mass traversed by crystals, and on removing the excess of carbonyl chloride by a stream of carbon dioxide, and treating the remaining mass with water, dimethylamidobenzoic acid separates out, and may be freed from adhering colouring matter by repeated washing with water, and further purified by crystallisation from hot alcohol. Its formation is represented by the equations:



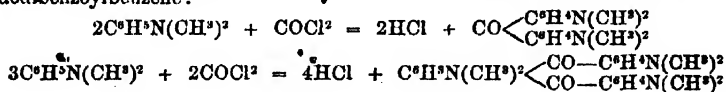
The acid prepared as above crystallises in short broad colourless needles, melts at 253° , dissolves in potash as well as in hydrochloric acid, but is insoluble in acetic acid, exhibiting therefore the characteristic properties of an amido-acid.

The same acid is produced by heating for three hours in a reflux apparatus 1 mol. para-amidobenzoic acid with 2 mols. methyl iodide and 3 mols. potassium hydroxide dissolved in methyl alcohol. It therefore belongs to the para-series.

Griess obtained the methylic ether of an isomeric dimethylamidobenzoic acid by the action of heat on the metameric compound benzbetaine or trimethyl-amidobenzoic acid, $\text{C}^6\text{H}(\text{CH}_3)_3\text{N}(\text{NH}_2)\text{COOH}$, and the homologous ether, methylic dimethyl-amido-anisate, $\text{C}^6\text{H}(\text{OCH}_3)\text{N}(\text{CH}_3)_2\text{COOCH}_3$, in like manner from trimethyl-amidanisic acid, $\text{C}^6(\text{OCH}_3)(\text{CH}_3)_2\text{NH}_2\text{COOH}$ (*2nd Suppl.* 187, 188).

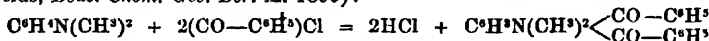
DIMETHYLANILINE, $\text{C}^6\text{H}^4\text{N}(\text{CH}_3)_2$. The reactions of this base with phosphorus trichloride, bromine, nitric acid, nitrous acid, and mercuric fulminate are described at p. 205.

Dimethylaniline heated with carbonyl chloride in a sealed tube to 50° , yields, as above stated, dimethyl-paramidobenzoic chloride; but at higher temperatures (120°) the products of the reaction are tetramethyl-diamidobenzophenone and hexmethyltri-amidodibenzoylbenzene:



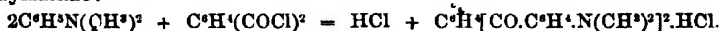
The former of these which constitutes the chief portion of the product is soluble in hydrochloric acid; the latter insoluble (Michler). See DIPHENYL KETONES.

Dimethylaniline and benzoyl chloride heated together in a sealed tube to 150° – 180° , or boiled together for several hours in a reflux apparatus, yield a crystalline mass from which ether extracts dimethylamidodibenzoylbenzene (Michler a. Dupertius, *Deut. Chem. Ges. Ber.* ix. 1899):



Dimethylaniline heated to 180° with perchloromethane, yields a carbotetradimethylaniline, $\text{C}[\text{C}^6\text{H}^4\text{N}(\text{CH}_3)_2]_4$, and when heated to 230° with chloroform, a methenyl-tridimethylaniline, $\text{CH}[\text{C}^6\text{H}^4\text{N}(\text{CH}_3)_2]_3$ (O. Fischer, *Deut. Chem. Ges. Ber.* v. 1235).

DIMETHYL - ANILINE - PHTHALEIN, $\text{C}^{14}\text{H}^{15}\text{N}^2\text{O}^2$, $\text{C}^6\text{H}_4\text{[CO.C}^6\text{H}^4\text{N}(\text{CH}_3)_2]_2$ (O. Fischer, *Deut. Chem. Ges. Ber.* ix. 1753; x. 952). The hydrochloride of this base is formed by the action of phthalic chloride on dimethylaniline:



On bringing the two bodies together, heat is evolved and the mixture becomes dark brown, and on heating it for a short time, the colour changes to yellow-green, a violet effervescence takes place, and the thickened mass becomes dark green. The reaction is accelerated by addition of small quantities of zinc-dust. After the frothing is over, water is added to prevent further decomposition, and the excess of dimethylaniline is distilled off with steam. The residue solidifies on cooling to a resin having a reddish surface-shimmer, and may be triturated to a dark green powder. The crude product, which dissolves easily and with green colour in alcohol, wood-spirit, chloroform, and acetic acid, sparingly in water, and scarcely at all in ether, is purified by boiling it several times with ether, dissolving it in a small quantity of alcohol, mixing the solution with water, and crystallising the resulting precipitate from chloroform.

Dimethylaniline-phthalein is obtained in the free state by the action of alkalis on

the hydrochloride, and separates in the form of greenish-white granules which become colourless on filtration, but green again when dry. It is also formed by the action of dehydrating agents (zinc chloride, phosphoric oxide, &c.) on a mixture of phthalic oxide and dimethylaniline.

The *monohydrochloride*, $C^2H^2N^2O^2.HCl$, crystallises in small needles having a greenish-yellow lustre. The *dihydrochloride*, $C^2H^2N^2O^2.2HCl$, is obtained as a yellowish-red, crystalline, extremely hygroscopic precipitate, when dry hydrogen chloride is passed into an ethereal solution of the base carefully dried with calcium chloride; also by dissolving the free base in hydrochloric acid. When heated on the water-bath, it gives off hydrogen chloride, and is converted into the green monohydrochloride.

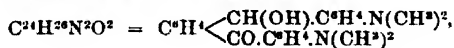
A *platino-chloride*, $2(C^2H^2N^2O^2.HCl).PtCl^4$, is obtained as a blue-green crystalline precipitate, when an alcoholic solution of platinic chloride is added to an alcoholic solution of the green hydrochloride; but when a solution of the base in strong hydrochloric acid is added to an alcoholic solution of platinic chloride, the salt $C^2H^2N^2O^2.2HCl.PtCl^4$ is obtained as a yellow-red crystalline precipitate easily soluble in water, sparingly in alcohol and ether.

The *picrate*, $C^2H^2N^2O^2.C^6H^3(NO^2)^3OH$, obtained like the platinum salt, is a dark green precipitate. A yellow picrate, $C^2H^2N^2O^2.2C^6H^3(NO^2)^3OH$, is formed when a solution of the yellow hydrochloride is added to aqueous picric acid. Some of the other salts of this base crystallise well.

Dimethylaniline-phthalein heated considerably above 200° with melting potash is resolved into dimethylaniline and phthalic acid.

A *hexnitro-derivative*, $C^2H^{10}(NO^2)^6N^2$, is formed by treating the phthalein with fuming nitric acid.

DIMETHYL-ANILINE-PHTHALIN.



is obtained by reduction of the corresponding phthalein with zinc-dust and glacial acetic acid, and purified by crystallisation from wood-spirit, from which it separates in crystalline grains easily soluble in alcohol and ether. The *picrate*, $C^2H^2N^2O^2.C^6H^3(NO^2)^3OH$, is a light yellow precipitate. The *platinochloride* is nearly colourless (Fischer, *Deut. Chem. Ges. Ber.* 3, 952).

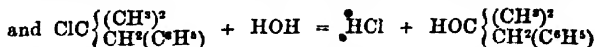
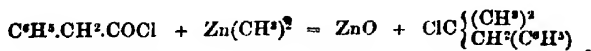
DIMETHYL-ANILINE-SULPHONIC ACID, $C^6H^4N(CH^3)^2.SO^2H$. See p. 235.

DIMETHYL-BENZAMIDE, $C^6H^5.CO.N(C^2H^5)^2$. See BENZAMIDE (p. 156).

DIMETHYL-BENZHYDROL, $C^{13}H^{10}O = C^6H^4(CH^3)---CHOH---C^6H^4(CH^3)$. See DITOLYL-CARBINOL.

DIMETHYL-BENZOPHENONE, $C^{13}H^{10}O = C^6H^4(CH^3)---CO---C^6H^4(CH^3)$. See DITOLYL KETONE.

DIMETHYL-BENZYL CARBINOL, $C^{11}H^{10}O = HOC \begin{Bmatrix} (CH^3)^2 \\ CH^2(C^6H^5) \end{Bmatrix}$. A tertiary alcohol obtained by treating phenylacetyl chloride with zinc-methyl, and the product with water, just as trimethyl-carbinol is obtained from zinc-methyl and acetyl chloride:



It crystallises in long needles, melts at $20^\circ-22^\circ$, and boils at $220^\circ-230^\circ$ (Popoff, *Deut. Chem. Ges. Ber.* viii. 768).

DIMETHYL-DIETHYLAMMONIUM IODIDE. See ETHYLAMINES.

DIMETHYL-DIETHYL-METHANE, $C^7H^{10} = C(CH^3)^2(C^2H^5)^2$. See HEPTANES (2nd Suppl. 643).

DIMETHYL-ETHYL-ACETIC ACID, $C(CH^3)^2(C^2H^5).COOH$. See CAPROIC ACIDS (p. 379).

DIMETHYL-ETHYLAMINE ETHIODIDE. See ETHYLAMINES.

DIMETHYL-ETHYL-BENZENE, $C^{10}H^{14} = C^6H^5(CH^3)^2(C^2H^5)$. See MESITYLENE, HOMOLOGUES OF.

DIMETHYL-ETHYL CARBINOL, $(CH^3)^2(C^2H^5).COH$, TERTIARY AMYL ALCOHOL. See 1st Suppl. 115; and p. 81 of this volume.

DIMETHYLENE-DIPHENYL-DIAMINE, $N^2(CH^2)(C^6H^5)^2$, appears to be formed when aniline is gently heated with excess of methylene iodide (Julie Lermontoff, *Deut. Chem. Ges. Ber.* vi. 1255).

DIMETHYL-HYDRAZINE. See HYDRAZINES.

$C^2H^{10}O = (OH)^2.CH^2.CH(OH)^2.CO.H$. See **HEPTYL ALCOHOLS**.

DIMETHYL-ISOPROPYL-CARBINOL, $C^8H^{14}O = (CH^3)^2.CH(CH^3)^2.CO.H$. See **HEXYL ALCOHOLS**.

DIMETHYL-ISOPROPYL-CARBAMINE. Syn. with **DIACETONALKAMINE** (p. 631).

DIMETHYL-MALONIC ACID, $C^8H^2(CH^3)^2O^4$. *B-Isopyrotartaric acid*. See **PYROTARTARIC ACIDS**.

DIMETHYL-OXALURAMIDE, $C^8H^8N^2O^3 = C^2O^2N(CH^3)[CO(CH^3)NH]H^2N$, is formed by the action of alcoholic ammonia at ordinary temperatures on dimethyl-parabanic acid. It melts at 225° , and is but slightly soluble in alcohol even at the boiling heat (Menschutkin, *Liebig's Annalen*, clxxviii. 201).

DIMETHYL-OXAMIDE, $C^2H^2(CH^3)^2N^2O^2$. See **OXAMIDE**.

DIMETHYL-PARABANIC ACID. See **PARABANIC ACID**.

L, $CH^3.C^6H^4.O^2H^4.CH^3$. See **DITOLYL**.

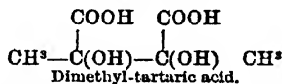
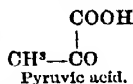
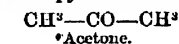
DIMETHYL-PHOSPHINIC ACID, $PH(CH^3)^2O^2 = PO(OH)(CH^3)^2$. See **PHOSPHINIC ACIDS** (2nd Suppl. 956).

DIMETHYL-PROPYLBENZENE, $C^{11}H^{16} = C^6H^5(CH^3)^2(C^2H^5)$. See **MESITYLENE**, **HOMOLOGUES OF**.

DIMETHYL-PROTOCATECHUIC or **VERATRIC ACID**, $C^8H^6(OCH^3)^2.CO^2H$. See **DIOXYBENZOIC ACIDS** (p. 290).

DIMETHYL-PURPURATIONTHIN. See **PURPURATIONTHIN**.

DIMETHYL-TARTARIC ACID, $C^8H^{10}O^4 = C^2H^4(CH^3)^2O^4$ (Boettinger, *Deut. Chem. Ges. Ber.* ix. 1064, 1621). This acid, formed by treating an alcoholic solution of pyruvic acid with granulated zinc (and a little hydrochloric acid) or with zinc dust, is related to pyruvic acid in the same manner as pinacone to acetone:



The *zinc salt* separates during the reaction in the form of a white substance, perfectly insoluble in cold water, while zinc lactate remains in solution, together with another zinc salt, which appears to belong to a modified pyruvic acid, and separates when the aqueous solution is boiled.

Dimethyltartaric acid is bibasic. The *acid potassium salt*, which is anhydrous, dissolves with great difficulty in cold water and only sparingly in hot water. From the hot saturated solution it separates on cooling in groups of hard transparent six-sided plates. The *neutral potassium salt* forms anhydrous needles, much more soluble in water either hot or cold than the acid salt. Its dilute solution forms with barium chloride a precipitate very slightly soluble in cold water, and with calcium chloride a precipitate almost insoluble in water. By very gradually mixing the neutral potassium salt with barium chloride, a *barium salt* is formed crystallising in rosettes of prismatic needles containing $3\frac{1}{2}$ mols. water, which it gives off at $180^\circ-200^\circ$. The *magnesium salt* is soluble. The *neutral copper salt* is sparingly soluble in water, easily soluble in dilute acids and in ammonia. The *lead salt* is insoluble in water. The potassium salt forms a precipitate with mercuric chloride.

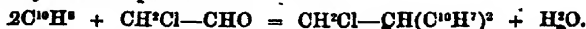
DIMETHYL-TOLYLOXYETHYLENEAMMONIUM. See **OXETHYLENE-TOLUIDINES**, under **TOLUIDINE**.

ITHIOPURPURIN. See **PURPURATIONTHIN**.

See **NAPHTHOLS**.

See **NAPHTHYL**.

The monochlorinated compound $\text{CH}^2\text{Cl}-\text{CH}(\text{C}^{10}\text{H}^7)^2$ is formed by the action of strong sulphuric acid on a mixture of monochloraldehyde and naphthalene:



When subjected to dry distillation it yields a non-solidifying oil, boiling above 360° , and apparently consisting of dinaphthylethylene, $\text{C}^2\text{H}^2(\text{C}^{10}\text{H}^7)^2$. With bromine it yields a viscid oil, the formation of which is attended with evolution of hydrobromic acid (Hepp, *Deut. Chem. Ges. Ber.* vii. 1419).

Dinaphthyl-trichlorethane, $\text{CCl}^3-\text{CH}(\text{C}^{10}\text{H}^7)^2$, is produced by mixing naphthalene, chloral, and sulphuric acid, at ordinary temperatures, and keeping the mixture well cooled. It then solidifies to a compact mass which, when washed with warm water, splits up into brittle whitish lumps. It melts under warm water, dissolves very sparingly in alcohol, but easily in ether, and on mixing the ethereal solution with alcohol, the dinaphthyl-trichlorethane gradually crystallises in small thick hexagonal plates (Grabowski, *ibid.* vi. 224).

Dinaphthyl-dichlorethylene, $\text{CCl}^2=\text{C}(\text{C}^{10}\text{H}^7)^2$, is formed by boiling dinaphthyltrichlorethane with alcoholic potash, and separates from solution in hot aniline in pointed crystals. It is slightly soluble in chloroform, carbon sulphide, and benzene, but aniline is the only solvent from which it crystallises well (Grabowski, *loc. cit.*)

DINAPHTHYL-KETONE, $\text{CO}(\text{C}^{10}\text{H}^7)^2$. See NAPHTHYL KETONES.

DINAPHTHYL-METHANE, $\text{C}^{20}\text{H}^{16} = \text{CH}^2(\text{C}^{10}\text{H}^7)^2$ (Grabowski, *Deut. Chem. Ges. Ber.* vii. 1605). This compound is formed by the action of sulphuric acid on a mixture of naphthalene and methylal:



As the action is apt to become violent, it is best to proceed as follows: A solution of 5 pts. naphthalene in 20 pts. chloroform is mixed with 1 pt. methylal; 10 pts. of strong sulphuric acid are added by small portions, with continual cooling and brisk agitation; and the mixture is left for twelve hours at ordinary temperatures, with frequent agitation. About 30 pts. of water are then added; the chloroform is distilled off; the residue collected on a cloth, washed, and boiled with ether; the product which remains on distilling off the ether is distilled from a retort till the temperature rises above 300° ; after which the retort is cooled, and the black pitchy mass is further distilled from a smaller retort. The distillate solidifies in contact with alcohol to a crystalline mass which is recrystallised from alcohol. At the first crystallisation, a brown oil is deposited, from which the clear solution must be decanted, a quicker purification being thus obtained. The yield of dimethyl-methane is not quite equal to the quantity of methylal employed.

Dinaphthyl-methane crystallises from alcohol in short colourless prisms, melts at 109° , distils without decomposition above 360° , and appears to be capable of withstanding a considerable temperature, inasmuch as the oily mass deposited in the first crystallisation yields, when passed through a red-hot tube filled with pumice, a considerable additional quantity of dinaphthyl-methane. The compound is very soluble in ether, chloroform, and benzene, and dissolves in about 15 pts. of boiling and 120 pts. of cold alcohol. It remains almost unaltered when heated with chromic acid mixture even for twenty hours. Fuming sulphuric acid converts it into a sulpho-acid. It is easily nitrated by nitric acid even at ordinary strength.

Dibromodinaphthylmethane, $\text{C}^{20}\text{H}^{16}\text{Br}_2$, is produced by adding 2 mols. bromine to an ethereal solution of 1 mol. dinaphthyl-methane cooled with water. The crude product is washed, first with cold, then with hot alcohol, and crystallised from a small quantity of benzene. In operating with small quantities, however, it is best, after dissolving the product in benzene to add about half the quantity of alcohol. The compound crystallises from the mixture of alcohol and benzene in warty groups of short colourless needles, melts at 190° , and partly decomposes when distilled. It is somewhat sparingly soluble in ether, benzene, and chloroform, much more freely in alcohol. It is not altered by boiling with alcoholic potash (Grabowski).

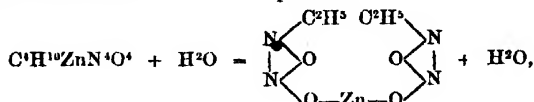
Tetranitrodinaphthylmethane, $\text{C}^{20}\text{H}^{12}(\text{NO}_2)^4$.—Dinaphthylmethane dissolves very quickly in 10 pts. of fuming nitric acid, and the solution, after ten or twelve hours, deposits the tetranitro-compound in small rhombic nearly colourless crystals, which may be purified by washing, and boiling with alcohol and glacial acetic acid. It acquires a golden yellow colour by exposure to light, melts at $260^\circ-270^\circ$ without perceptible decomposition and detonates slightly at a higher temperature. It is nearly insoluble in alcohol, ether, chloroform, benzene, and glacial acetic acid, but dissolves with moderate facility in aniline (Grabowski).

Dinaphthylmethane-picric acid, $C^{22}H^{10}.2C^2H^2(NO^2)_3OH$, is obtained by dissolving 1 mol. dinaphthylmethane and 2 mols. picric acid, each in the smallest possible quantity of chloroform, and mixing the two solutions. The liquid on cooling deposits the acid in reddish-yellow prisms, which must be washed with chloroform. It melts at 142° – 143° , detonates slightly when heated, and is easily decomposed by alkalis (Grabowski).

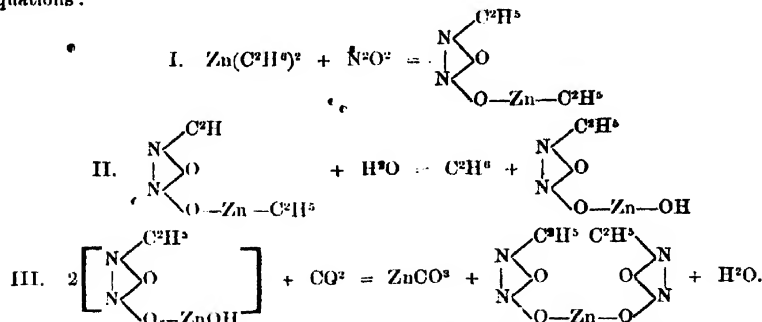
DINAS. On the so-called 'Plastic Dinas Crystal,' see Bischoff (*Dingl. pol. J.* cccxi. 345; *Chem. Soc. Jour.* 1877, i. 354).

DINITROETHYLIC ACID, $C^2H^2N^2O^2$. This acid, discovered by Frankland (iv. 61), has been further examined by Zuckschwerdt (*Deut. Chem. Ges. Ber.* vii. 291; *Liebig's Annalen*, clixiv. 302). The zinc salt was prepared by a method essentially the same as that of Frankland, but without the use of a high-pressure apparatus. Zinc-ethyl mixed with ether was introduced into a small flask filled with dry nitrogen dioxide, and connected by a series of drying tubes with a gas-holder containing the same gas. The contents of the flask, consisting of a white crystalline mass, were then gradually decomposed by water, and when the evolution of the ethane thereby produced had ceased, the solution was completely precipitated by carbonic acid, afterwards boiled for a short time, filtered, evaporated over the water-bath, and the residue dried over sulphuric acid.

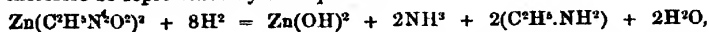
The zinc-salt thus obtained has the composition :



and forms large, colourless, well-defined thick prismatic crystals belonging to the orthorhombic system. Their mode of formation is represented by the following equations :



The zinc salt was reduced in a capacious vessel by nascent hydrogen, evolved either from sodium-amalgam and water, or from a mixture of finely divided iron, zinc, and dilute aqueous potash; the evolved gases and vapours were absorbed by hydrochloric acid; the solution freed from excess of the latter by evaporation on the water-bath; and the dried salts were exhausted with a mixture of absolute alcohol and a small quantity of ether. The residue thus obtained consisted of ammonium chloride, and the solution contained ethylamine. The action of nascent hydrogen on the zinc salt may therefore be represented by the equation :



and the products show that in dinitroethyllic acid, the alcohol-residue is in direct combination with the nitrogen, as represented in the constitutional formula above given.

DIORITE. The following analyses of the rock have lately been published : 1. Diorite from Gympie in Queensland, containing hornblende, plagioclase, and orthoclase, with small quantities of mica and iron pyrites : a. Total constituents; b. Soluble in hydrochloric acid (54.775 per cent.); c. Insoluble in hydrochloric acid (45.225 per cent.). The quartz veins of this rock are rich in gold (Daintree, *Geol. Soc. Q. J.* xxviii. 271). 2–5. Diorites from the Baden Black Forest (Vogelgesang, *Jahresb. f. Chem.* 1873, 1217). 2. Granular distinctly mixed diorite from the Willmendorf near Oberglotterthal. 3. Slaty, distinctly micaceous diorite from the Huloehhof near

DIORTHOCRESYLAMINE--DIOXYPHENYLETHYLENE. 655

St. Peter. 4. Red green-speckled *diorite-aphanite* from the pit at St. Margen. 5. Dark *aphanite-slate* from the Tafelbühl at Yach. 6. *Quartziferous diorite* containing a small quantity of orthoclase with much *plagioclase*, mica, hornblende and quartz, from the Pauli Thal in the Bannat (Niedzwiecki, *Jahresb.* 1873, 1218).

	1			2	3	4	5	6
	a	b	c					
SiO ²	50.50	41.94	60.86	48.4	48.5	53.8	51.8	65.71
P ² O ⁵	—	—	—	0.69	1.24	0.04	0.2	—
Al ² O ³	18.49	19.56	17.19	27.7	19.0	13.5	8.6	17.08
Fe ² O ³	1.47	2.68	—	—	—	18.8	24.8	2.84
FeO	6.44	7.79	5.18	7.5	9.54	—	—	1.79
CaO	8.80	10.09	7.24	9.2	12.3	7.6	7.6	5.24
MgO	8.53	9.94	6.82	trace	2.6	1.7	0.8	2.57
K ² O	0.64	0.21	1.03	1.5	1.9	1.69	0.96	1.02
Na ² O	1.65	2.00	1.23	4.9	5.2	2.92	2.33	3.87
S	0.19	0.35	—	—	—	—	—	—
CO ²	0.82	1.40	—	—	—	—	—	—
H ² O (combined)	1.60	2.92	—	—	—	—	—	—
H ² O (hygroscopic)	0.85	1.55	—	1.6	0.69	2.0	1.7	—
	99.98	100.43	99.55	101.49	100.97	101.95	98.69	100.12

On the Diorites of the Ehrenberg near Ilmenau and their constituent minerals, see E. E. Schmid (*Jahrb. f. Min.* 1876, 136; *Jahresb. f. Chem.* 1876, 1287).

On the Diorites of Minnesota, see Streng & Kloos (*Jahrb. f. Min.* 1877, 113-138; *Chem. Soc. Jour.* 1877, ii. 721).

See TOLUIDINES.

See TOLUIDINES.

DIOXINDOL. See INDOL.

DIOXYADIPIC ACID. See ADIPIC ACID (2nd Suppl. 29).

DIOXYANTHRAQUINONES. See ANTHRAQUINONE (pp. 100-109).

DIOXYBENZENES. See PHENOLS.

DIOXYBENZENE-DISULPHONIC ACID, C⁶H²(OH)²(SO³H)². See BENZENEDISULPHONIC ACID (p. 258).

DIOXYBENZZOIC ACIDS, C⁶H⁴(OH)².COOH (pp. 288-292).

DIOXYBUTYRIC ACID, C⁴H⁶O⁴. See OXYBUTYRIC ACIDS.

DIOXYCINCHONIDINE, C²⁰H²⁴N²O⁸. See CYNCHONIDINE (p. 487).

DIOXYMALEIC ACID. See MALEIC ACID.

DIOXYMALONIC ACID. See MALONIC ACID.

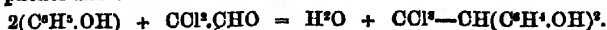
DIOXYNAPHTHALENES. See NAPHTHALENES.

DIOXYPHENYLETHYLENE, C¹⁴H⁸O² = CH²=C(C⁶H⁴.OH)² (E. ter Meer, *Deut. Chem. Ges. Ber.* vii. 1200). This compound is formed by boiling an alcoholic solution of dioxyphenyltrichlorethane (*infra*) with zinc-dust. The product, which is usually free from chlorine after twenty-four hours' boiling, is filtered from zinc, the zinc boiled with alcohol to extract the remainder, the greater part of the alcohol distilled off, the brown product poured into water, and the resulting precipitate crystallised from glacial acetic acid.

Dioxyphenylethylene forms small white crystals which melt at 280° with partial decomposition. It is easily soluble in alcohol, ether, and hot glacial acetic acid, less soluble in benzene, sparingly in carbon disulphide. It dissolves also in dilute potash-ley, and the solution when evaporated leaves crystals of the potassium compound.

Diacetyl-dioxyphenylethylene, CH²=C(C⁶H⁴.O.CO²H³O)², is formed by boiling dioxyphenylethylene with acetic anhydride. It is somewhat sparingly soluble in hot alcohol, ether, benzene, glacial acetic acid, and acetone, nearly insoluble in cold alcohol, and melts at 213°.

DIOXYPHENYLTRICHLORETHANE, $C^{12}H^{11}Cl^3O^2 = CCl^3 \cdot CH(C^6H^4.OH)^2$ (ter Meer, *loc. cit.*) This compound is prepared by the action of sulphuric acid on a mixture of phenol and chloral:



A mixture of 2 mols. phenol and 1 mol. chloral cooled with iced water, is treated with an equal volume of a mixture of 3 vols. sulphuric acid and 1 mol. glacial acetic acid; the mixture is taken out of the iced water; and as soon as it becomes warm and red and a strong reaction is set up, it is stirred into a large quantity of cold water. The viscid, red, or violet mass thereby separated, which becomes solid after washing and several days' contact with water, is digested with water on the water-bath till the odour of phenol disappears, then crystallised from a mixture of benzene and alcohol, and the crystals thereby separated are washed with cold benzene.

Dioxyphenyltrichlorethane forms small white crystals, melts with decomposition at 202° , dissolves easily in alcohol, ether, glacial acetic acid, hot benzene and toluene, sparingly in cold benzene. Boiling alcoholic potash solution dissolves it with red colour and separation of potassium chloride, and acids added to the solution throw down a red greasy product. Dioxyphenyltrichlorethane is decomposed by heating with sulphuric acid, and is easily nitrated by nitric acid.

Diacetyl-dioxyphenyltrichlorethane, $CCl^3-CH(C^6H^4-O-C^2H^3O)^2$, formed by boiling the preceding compound with acetic anhydride, crystallises from alcohol in radiate groups of small needles which melt at 138° (ter Meer).

DIOXYRETISTENE, $C^{16}H^{14}O^2$, is one of the products formed by oxidation of retene with chromic acid. Fuming sulphuric acid converts it into a sulpho-acid which forms well-defined salts (Ekstrand, *Bull. Soc. Chim.* [2], xxiv. 55).

DIOXYTHYMYLETHANE, $C^{12}H^{10}O^2 = CH^3-CH(C^{10}H^{12}OH)^2$ (E. Jäger, *Chem. Soc. J.* 1877, i. 262; A. Steiner, *Deut. Chem. Ges. Ber.* xi. 287). This compound is obtained: 1. Together with dioxythymylethylene, by heating dioxythymyltrichlorethane (*supra*) with zinc-dust. By boiling the alcoholic solution of the chlorine-compound with zinc-dust, then distilling off the alcohol, and pouring the viscid residue into water, a white glutinous mass is obtained, which quickly solidifies and turns red in contact with the air; and on washing this mass with very cold glacial acetic acid, there remains a white residue which, after several recrystallisations, is obtained in small cubes having nearly the composition of a compound of dioxythymylethane with 1 mol. acetic acid, $C^{12}H^{10}O^2.C^2H^3O^2$. On heating this compound to $138^\circ-140^\circ$, the whole of the acetic acid is driven off and dioxythymylethane remains behind. The mother-liquors of the several crystallisations yield dioxythymylethylene (Jäger). 2. By adding a mixture of chloroform and stannic chloride to a well-cooled mixture of thymol (50 pts. by weight), and para-aldehyde (10 pts. by weight). The yellow viscous mass so obtained is freed from thymol by distilling in a current of steam; and by crystallising the solid residue from hot benzene, dioxythymylethane is obtained in the form of small white needles (Steiner).

Dioxythymylethane crystallises from alcohol in large plates which effloresce on exposure to the air. It melts at 185° (Steiner); at 180° (Jäger); is easily soluble in cold alcohol, methyl alcohol, ether, and chloroform, less easily in cold benzene, and almost insoluble in boiling petroleum-ether. It distils without decomposition; dissolves more easily in hot caustic potash than in cold, and is precipitated from this solution by acids (Steiner).

Diacetyldioxythymylethane, $C^{12}H^{10}O^4 = CH^3-CH(C^{10}H^{12}OC^2H^3O)^2$, is prepared by heating dioxythymylethane and acetic anhydride at $160^\circ-170^\circ$ for several days. It crystallises from alcohol in small colourless needles melting at 100° , and may be distilled without decomposition; dissolves easily in cold alcohol, ether, acetone, chloroform, and benzene, also in hot petroleum ether, but is insoluble in water (Steiner).

Dibenzoyldioxythymylethane, $C^{18}H^{18}O^4 = CH^3-CH(C^{10}H^{12}OC^7H^5O)^2$, is prepared by heating dioxythymylethane and benzoyl chloride for several hours at 150° . It crystallises from boiling alcohol in colourless needles which melt at 191° ; dissolves easily in chloroform, in hot alcohol, ether, and acetone, less easily in cold; distils without decomposition (Steiner).

Diethyldioxythymylethane, $C^{14}H^{18}O^2 = CH^3-CH(C^{10}H^{12}OC^2H^5)^2$, is formed by heating on a water-bath an alcoholic solution of dioxythymylethane with the calculated quantities of ethyl iodide and potassium hydrate in a flask connected with a reversed condenser. It crystallises from alcohol in tufts of needles which melt at 72° ; at 100° these crystals give up the alcohol of crystallisation they contain, and form a viscous mass which solidifies finally to a porcelain-like mass. The compound is insoluble in water, easily soluble, however, in alcohol, ether, chloroform, acetone, petroleum-ether, and methyl-alcohol (Steiner).

Dioxythymylethane and the diacetyl-compound yield thymoquinone when oxidised by a mixture of manganese dioxide and sulphuric acid, (Steiner).

Dioxythymyltrichlorethane, $C^{10}H^{12}Cl^3O^2 = OCl^2-CH(C^{10}H^{12}OH)^2$, is obtained by dissolving 1 mol. chloral in 2 mols. thymol, and gradually stirring into the well-cooled solution from 4 to 5 times its amount of strong sulphuric acid diluted with a third of its volume of glacial acetic acid. The liquid then gradually deposits a white resinous mass, which in contact with water soon becomes solid and granular. The well-washed product is boiled with water, if necessary, with the aid of superheated steam, till it no longer smells of thymol, then crystallised several times from alcohol, whereby spicular monoclinic crystals are obtained, consisting of a compound of dioxythymyltrichlorethane with 1 mol. alcohol, $C^{10}H^{12}Cl^3O^2.C^2H^4O$.

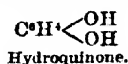
Dioxythymyltrichlorethane is easily soluble in alcohol, ether, acetone, and wood-spirit, insoluble in water and in cold dilute potash solution, but is blackened and decomposed by potash in warm or concentrated solution. With nitric acid it forms a nitro-compound difficult to purify by recrystallisation. The two hydroxyls in the compound are easily replaced by the action of acetic anhydride or benzoyl chloride. By heating with zinc-dust it is reduced, as already observed, to dioxythymylethane and dioxythymylethylene (Jäger, *Deut. Chem. Ges. Ber.* vii. 1197).

DIOXYTHYMLETHYLENE, $C^{10}H^{12}O^2 = (C^{10}H^{12}.OH)^2C=CH^2$, is formed, together with dioxythymylethane, by heating dioxythymyltrichlorethane with zinc-dust, and may be obtained pure by repeated fractional crystallisation from the mother-liquors of dioxythymylethane, and especially from the acetic acid with which the crude product has been washed. It forms needle-shaped crystals melting at $170^\circ-171^\circ$, easily altered by light, rather more soluble in the usual solvents than the ethane-compound, but, like the latter, it is quite insoluble in water.

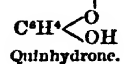
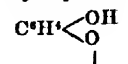
Weak oxidising agents exert a most remarkable action on this body. Its alcoholic solution, treated with potassium ferricyanide, yields green crystals which have the composition $C^{14}H^{10}O^4$, melt at $214^\circ-215^\circ$, and resist the action of nearly all solvents except toluene and chloroform, from which they may be recrystallised, though with considerable loss.

If, before adding the ferricyanide, the solution is rendered alkaline with a small quantity of sodium carbonate or ammonia, the green crystals are no longer formed, but a red flocculent precipitate falls down; and this when dissolved in chloroform is deposited in the form of dark red crystals having the composition $C^{12}H^{10}O^2$, melting to a brown liquid at 215° , easily soluble in chloroform, but nearly insoluble in all other solvents, and easily decomposed by acids and alkalis, even when very dilute.

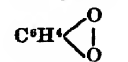
A mixture of dioxythymylethylene and the red crystals, dissolved in chloroform, deposits on evaporation the green needles above described. Hence, and from the formula, it appears that dioxythymylethylene and the two products of its oxidation are related to one another in the same manner as hydroquinone, quinone, and quinhydrone; the red crystals may therefore be called dioxythymylquinonethylene, and the green crystals dioxythymylquinhydroneethylene:



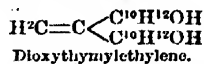
Hydroquinone.



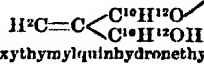
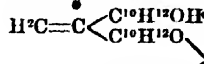
Quinhydrone.



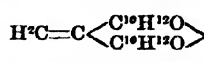
Quinone.



Dioxythymylethylene.



Dioxythymylquinhydroneethylene



Dioxythymylquinonethylene.

The quinone can be easily reduced to dioxythymylethylene by sulphurous acid in the cold, if suspended in the original flocculent state in alcohol, but when once crystallised, it requires boiling in order to dissolve it. At a temperature of 100° , however, the sulphuric acid formed by the reaction proves sufficient to effect the partial decomposition of the substance, and only a small quantity of dioxythymylethylene is formed, together with a large quantity of a resinous matter. A better method, however, is to reduce the quinone with zinc-dust and acetic acid, as in this way the formation of resinous matter is avoided.

By means of this reaction pure dioxythymylethylene can easily be produced. It is only necessary to treat the impure mixture of dioxythymylethylene and dioxythymyl-

ethane, obtained by the action of zinc-dust on dioxythymyltrichlorethane, with weak oxidising agents, which act only on the ethylene-compound, and convert it into the insoluble quinhydrone, which is then again reduced as above described (Jäger).

See DIPHENYL.

DIPARACHLOROPHENYLTHIOCARBAMIDE, $\text{CO}(\text{NC}^6\text{H}^4\text{Cl.H})^2$, is formed as a secondary product in the preparation of parachlorophenyl-thiocarbimide, $\text{CS}(\text{N.C}^6\text{H}^4\text{Cl})$, by the action of phosphorus anhydride, or of iodine, on the corresponding thiocarbamide (*infra*). It crystallises only from glacial acetic acid, and then forms long needles. It dissolves apparently without alteration in strong sulphuric acid, and volatilises without previous fusion at 270° , being partly decomposed at the same time (Beilstein a. Kurbatow, *Liebig's Annalen*, clxxvi. 46).

Diparachlorophenyl-thiocarbamide, $\text{CS}(\text{NC}^6\text{H}^4\text{Cl.H})^2$, is formed by prolonged boiling of parachloraniline with carbon disulphide and absolute alcohol. It crystallises in needles melting at 168° (Beilstein a. Kurbatow).

DIPARACRETYLAMINE. See TOLUIDINES.

DIPARAPICTYLAMINE. See NITRANILINES under BENZENES, AMIDO- (p. 199).

DIPHENIC ACID, $\text{C}^6\text{H}^{10}\text{O}^4 = \text{C}^6\text{H}^4\text{.CO}^2\text{H} - \text{C}^6\text{H}^4\text{.CO}^2\text{H}$. This acid, produced by oxidation of phenanthrene-quinone, has been already described (*2nd Suppl.* 434). *Ethyllic Diphenate*, $\text{C}^{12}\text{H}^8(\text{CO}^2\text{C}^2\text{H}^5)^2$, is prepared by treating a solution of the acid in absolute alcohol with hydrochloric acid, and precipitating with water. The ether, purified in the ordinary way, is a heavy limpid liquid, partially decomposed by distillation, not decomposed by boiling with water (Ostermayer, *Deut. Chem. Ges. Ber.* vii. 1091).

Dibromodiphenic acid, $\text{C}^6\text{H}^4\text{Br}^2\text{O}^4$, is produced by oxidising dibromophenanthrenequinone with potassium chromate and dilute sulphuric acid. The oxidation is slow and the dibromodiphenic acid separates very gradually on the surface of the liquid in the form of a nearly white powder. When purified by solution in ammonia, precipitation with hydrochloric acid, and recrystallisation from alcohol, it forms good crystals, melting at 295° – 296° , nearly insoluble in cold water, very sparingly soluble in hot water, somewhat soluble in alcohol and ether. It has a bitter taste, and reacts with metallic salts like diphenic acid. The barium and calcium salts crystallise in very thin scales, slightly soluble in water and in alcohol (Ostermayer, *Deut. Chem. Ges. Ber.* vii. 1091).

Dinitrodiphenic acid, $\text{C}^6\text{H}^4(\text{NO}^2)^2\text{O}^4 = \text{C}^6\text{H}^4(\text{NO}^2)\text{.CO}^2\text{H} - \text{C}^6\text{H}^4(\text{NO}^2)\text{.CO}^2\text{H}$. An acid of this composition is formed by the action of powerful oxidising agents on dinitrophenanthraquinone. It is a white powder, slightly soluble in ether and in cold water, more soluble in hot water and in alcohol. Its *barium salt*, $\text{C}^6\text{H}^4(\text{NO}^2)^2\text{O}^4\text{Ba} + 6\text{H}^2\text{O}$, forms long prismatic crystals; the *silver salt* is a white powder (R. Struve, *Deut. Chem. Ges. Ber.* x. 75).

Diamidodiphenic acid, $\text{C}^6\text{H}^4(\text{NH}^2)^2\text{O}^4 = \text{C}^6\text{H}^4(\text{NH}^2)\text{.CO}^2\text{H} - \text{C}^6\text{H}^4(\text{NH}^2)\text{.CO}^2\text{H}$, formed by the action of reducing agents on the nitro-acid, is a white amorphous powder melting at 250° – 251° . It is but slightly soluble in the ordinary solvents, but its ammonium salt is very soluble in water. Its hydrochloride heated with soda-lime yields a diamido-diphenyl, $\text{C}^{12}\text{H}^8(\text{NH}^2)^2$, which melts at 155° – 157° , and is therefore isomeric with benzidine (m.p. 118°). This diamidodiphenyl forms with *potassium ferricyanide* a blue precipitate insoluble in hot water and in acids, and gives with *chlorine-water*, first a blue, then a green, and finally a reddish-brown coloration (Struve).

Griess obtained *meta*-diamidodiphenic acid, $(\text{CO}^2\text{H} : \text{NH}^2 = 1 : 3)$, (convertible into benzidine), by reduction of metazoxybenzoic acid, and the ortho-modification, by the action of ammonia and acetic acid on the hydrochloride of orthohydrazobenzoic acid (p. 277). The structure of the diamidodiphenic acid obtained by Struve has not been exactly determined, but it is certainly not the meta-modification.

DIPHENOL, syn. with Dioxydiphenyl, $\text{C}^{12}\text{H}_{10}\text{O}^2 = \text{C}^6\text{H}^4\text{OH} - \text{C}^6\text{H}^4\text{OH}$ (see DIPHENYL). The same name has been applied, though less appropriately, to Oxydiphenyl, $\text{C}^{12}\text{H}^{10}\text{O} = \text{C}^6\text{H}^4 - \text{C}^6\text{H}^4\text{GH}$ (*2nd Suppl.* 938).

DIPHENYL, $\text{C}^{12}\text{H}^{10} = \text{C}^6\text{H}^5 - \text{C}^6\text{H}^5$. *Occurrence and Formation*.—Diphenyl has been detected by E. Büchner (*Deut. Chem. Ges. Ber.* viii. 22) in coal-tar. It was separated by subjecting the portions which distilled over at intervals of 5° between 242° and 263° , to the action of a low temperature, pressing the solidified mass, and recrystallising it from alcohol.

Diphenyl is formed, together with anthracene, chrysene, hydrocyanic acid, ammo-

nia, ammonium cyanide, and free carbon, when azobenzene is passed through red-hot tubes (Claus a. Suckert, *Deut. Chem. Ges. Ber.* viii. 37).

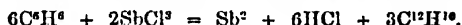
Preparation.—According to G. Schultz (*Liebig's Annalen*, clxxiv. 201), the quantity of diphenyl obtained by Fittig's method (action of sodium on a mixture of benzene and bromobenzene, iv. 409) amounts to between 9 and 12·7 per cent. of the benzene used, or 16·6 per cent. of the bromobenzene decomposed. A better yield is obtained by Berthelot's method of passing benzene vapour through a red-hot tube (1st *Suppl.* 918). If the benzene be distilled at the rate of 100 to 200 grams per hour, through an iron tube heated to bright redness, but not to an intense white heat, the yield is about 30 per cent.

When diphenyl is prepared by Fittig's method, a high-boiling thick oil containing bromine is obtained as bye-product. On standing, long white needles separate out, consisting of $C^{12}H^{12}$. The same body, which melts at 196° , is also produced by acting on the oil with sodium.

The bye-products contained in the diphenyl obtained by the method of Berthelot consist of Berthelot's *chrysene*, *benzerythrene*, and *bitumene* (1st *Suppl.* 261). The *chrysene* is a mixture of two modifications of diphenylbenzene, $C^{16}H^{14}$ (p. 665), and a yellow oil. The production of the former may be explained by the equation, $3C^6H^6 = C^{16}H^{14} + 2H^2$, or else by $C^6H^6 + C^{12}H^{10} = C^{16}H^{14} + H^2$; but the latter equation is not very probable, as only an insignificant quantity of diphenylbenzene is obtained by passing a mixture of benzene and diphenyl through a red-hot tube.

H. Lüddens (*Ber.* viii. 870) recommends a modification of Berthelot's process, which consists in passing a mixture of benzene vapour and carbon dioxide through an iron tube filled with fragments of pumice, and heated to bright redness in an ordinary gas combustion furnace; when the process is thus conducted, only a very small quantity of charcoal is deposited in the tube.

Watson Smith (*Chem. Soc. J.* 1878, ii. 30) prepares diphenyl by passing benzene-vapour mixed with antimonious or stannic chloride through a red-hot tube (see also Aronheim, *Ber.* ix. 1878). With *antimonious chloride* the reaction is:



By repeating the distillation several times, a quantity of diphenyl is obtained, much larger than that which results from the use of benzene alone, but still considerably below the theoretical amount. With *stannic chloride* the two following reactions take place:



and



By this method diphenyl is obtained in large quantity, and is found in the receiver in solid cakes consisting of a mixture of diphenyl with stannous chloride, the latter of which may be removed by hydrochloric acid. This is undoubtedly the quickest method of preparing diphenyl.

Diphenyl may also be prepared by heating phenol with potassium to 240° , and precipitating with water:



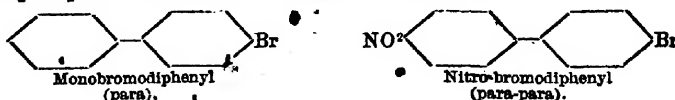
or by decomposing monobromobenzene with the current of a battery of two Bunsen's elements, the positive electrode being formed of sodium or zinc (Christomanos, *Gazz. chim. ital.* 1875, 402).

Properties and Reactions.—Diphenyl melts at $69\cdot6^{\circ}$, and boils at $238\cdot5^{\circ}$ (Christomanos). Heated in a stream of *chlorine* in presence of *iodine*, it is converted into perchlorodiphenyl, $C^{12}Cl^{10}$ (Ruoff, *Ber.* ix. 1048). Chlorine, in presence of $SbCl^3$, converts diphenyl into parachlorodiphenyl and parachlorodiphenyl (Kramers, *Liebig's Annalen*, clxxxix. 142). A mixture of diphenyl and *ethylene*, passed into the state of vapour through a red-hot tube, yields a mixture of benzene, cinnamene, anthracene, and phenanthrene, together with unaltered diphenyl (Barbier, *Ann. Ch. Phys.* [5], vii. 532).

SUBSTITUTION-DERIVATIVES OF DIPHENYL.

Diphenyl, subjected to the action of halogens, nitric acid, and sulphuric acid, yields mono- and di-substitution-derivatives. In the former, such as $C^{12}H^{11}Br$, $C^{12}H^{11}(NO^2)$, $C^{12}H^{10}(SO^2H)$, the substituted radicles mostly stand to the place of junction of the two benzene-nuclei in the para-position. The di-derivatives are known in

two modifications, the most frequent being those in which both the substituted groups are in the para-position relatively to the point of junction :



By oxidation with chromic anhydride, the monosubstituted diphenyls yield para-derivatives of benzoic acid, the group $\text{C}^6\text{H}^4\text{Br}$, for example, being oxidised to (1 : 4) bromobenzoic acid, while the other group (C^6H_5) is broken up. The di-derivatives, on the other hand, are converted by oxidation into two para-derivatives of benzoic acid, e.g. $\text{C}^6\text{H}^4(\text{NO}_2)\text{C}^6\text{H}^4\text{Br}$ into *p*-nitro and *p*-bromobenzoic acid.

G. Schultz (*Liebig's Annalen*, clxiv. 201) has further examined the mono-derivatives already described (2nd Suppl. 937), together with several di-derivatives. Some of these compounds have also been examined by Osten (*Deut. Chem. Ges. Ber.* vii. 170).

Mono-derivatives.

Bromodiphenyl, $\text{C}^{12}\text{H}^9\text{Br} = \text{C}^6\text{H}_5 - \text{C}^6\text{H}^4\text{Br}$, is formed by adding the calculated quantity of bromine to a solution of diphenyl in carbon sulphide, kept cold until the first reaction is over, and then heated on a water-bath as long as hydrobromic acid escapes. By fractional distillation and crystallisation from alcohol it is separated from unaltered diphenyl and dibromodiphenyl. It is moderately soluble in cold alcohol, more freely in hot alcohol and acetic acid, and very easily in ether, carbon sulphide, ethyl bromide, and benzene. From alcohol it crystallises in thin plates, melting at 89° , boiling at 310° , and smelling like oranges. On oxidising it with a solution of chromic trioxide in acetic acid, it yields parabromobenzoic acid.

Chlorodiphenyl, $\text{C}^{12}\text{H}^9\text{Cl}$, is obtained by distilling diphenylsulphonic acid with potash—whereby it is converted into dioxydiphenyl or diphenol, $\text{C}^{12}\text{H}_8(\text{OH})_2$ —and heating the latter with phosphorus pentachloride. It is freely soluble in alcohol and ether, and forms crystals melting at 75° and smelling like oranges. By oxidation it yields parachlorobenzoic acid.

Nitrodiphenyl, $\text{C}^{12}\text{H}^9\text{NO}_2$, is prepared by boiling 5 pts. of the hydrocarbon with 10 pts. of glacial acetic acid, and 4 of concentrated nitric acid, or by treating 2 pts. of diphenyl with 3 of the acid in the cold. It is sparingly soluble in cold, more freely in hot alcohol, and crystallises in long needles, melting at 113° , and boiling at 340° . On oxidation it yields paranitrobenzoic acid, and by reduction it is converted into para-amidodiphenyl, $\text{C}^{12}\text{H}^{10}\text{NH}_2$, Hofmann's xenylamine (Schultz). According to Lùddens (*Ber.* viii. 870) the process above described yields *ortho*- as well as *para*-nitrodiphenyl. He prepares the two modifications by mixing a solution of 15 grams diphenyl in 60 grams of glacial acetic acid, heated to about 60° , with a nearly cold mixture of 48 grams fuming nitric acid and 48 grams glacial acetic acid. The para-modification then crystallises out first, and the last mother-liquor contains a considerable quantity of the *ortho*-compound. The latter separates at winter temperature from an alcoholic solution diluted as much as possible with water, in light yellow, nearly colourless crystals, which gradually grow to moderately broad and thick plates about an inch long. It melts at 37° (Schultz).

Acetamidodiphenyl, $\text{C}^{12}\text{H}^{11}(\text{NH}.\text{C}^2\text{H}_5\text{O})$, obtained by prolonged boiling of amidodiphenyl with glacial acetic acid, crystallises in long shining needles easily soluble in alcohol and melting at 167° (Schultz).

Cyanodiphenyl, $\text{C}^{12}\text{H}^9\text{N} = \text{C}^6\text{H}_5 - \text{C}^6\text{H}^4(\text{CN})$, is prepared by heating an intimate mixture of dry potassium diphenylmonosulphonate, $\text{C}^6\text{H}_5.\text{C}^6\text{H}_4(\text{SO}^3\text{K})$, with potassium cyanide in a stream of dry carbon dioxide; the cyanodiphenyl then condensing in the cold part of the tube. It crystallises from alcohol in hard compact colourless crystals, is insoluble in water, dissolves very easily in alcohol and in ether, melts at 84° – 85° , and volatilises without decomposition (Doebner, *Liebig's Annalen*, clxxii. 109).

Oxydiphenyl, $\text{C}^{12}\text{H}^{10}\text{O} = \text{C}^6\text{H}_5 - \text{C}^6\text{H}^4(\text{OH})$. This compound is formed by fusing potassium diphenylmonosulphonate with potash; and, together with potassium oxydiphenyldisulphonate, by the action of heat on potassium oxydiphenylmonosulphonate; also by the action of potassium nitrite on the monoamidodiphenylsulphonate. It crystallises in felted microscopic needles, melts at 164° – 165° , boils without decomposition at 305° – 308° , and volatilises with vapour of water (Latschinoff, *Deut. Chem. Ges. Ber.* vi. 193).

Benzoyl-oxydiphenyl, $\text{C}^{12}\text{H}^9(\text{C}^7\text{H}_5\text{O})\text{O}$, formed by the action of benzoyl chloride on oxydiphenyl, crystallises in elongated tables with re-entering angles, melting at

152° (not at 132° as stated in 2nd Suppl. 938), dissolves sparingly in alcohol and ether, easily in boiling benzene containing toluene.

Nitro-oxydiphenyls, $C^{12}H^4(NO^2)OH$ and $C^{12}H^4(NO^2)_2OH$, are formed by gently heating 3 pts. of oxydiphenyl with 4 pts. nitric acid of sp. gr. 1.2; and on distilling the product with water, the *mononitro*-compound passes over alone. It crystallises in lemon-yellow prisms or laminae with re-entering angles, melts at 67°, sublimates at 110°, and dissolves easily in alcohol and ether. In aqueous alkaline carbonates it dissolves without evolution of carbon dioxide, forming unstable red compounds, which in drying, and partly in dissolving in water, give up mononitro-oxydiphenyl. From the potassium-compound, ether extracts the nitro-oxydiphenyl even in presence of potassium carbonate.

Dinitro-oxydiphenyl, $C^{12}H^4(NO^2)_2OH$, crystallises in golden-yellow laminae or elongated tables, which melt at 154°, and dissolve with difficulty in alcohol, ether, and benzene. On heating the compound with solution of potassium carbonate, a sparingly soluble potassium salt, $C^{12}H^4(NO^2)_2OK + 2H^2O$, is formed, which crystallises in annular groups of laminae (Latschinoff).

Di-derivatives.

Dibromodiphenyl, $C^8H^4Br-C^8H^4Br$, obtained by triturating diphenyl or mononitrodiphenyl with bromine and water, is a liquid which boils without decomposition at 355°–360°, and has a pleasant odour of oranges. Dissolved in glacial acetic acid and oxidised by chromic acid, it yields *parabromobenzoic acid*. The same dibromodiphenyl is obtained by heating the diazoperbromide prepared from benzidine or diamidodiphenyl, which has its two amidogen-groups in the *para*-position with respect to the point of junction (1st Suppl. 210): hence it follows that this dibromodiphenyl is also a *para-para*-compound.

Bromonitrodiphenyl, $C^{12}H^4BrNO^2$, is obtained by heating equal parts of bromodiphenyl and concentrated nitric acid, exhausting the crude products several times with boiling alcohol, and crystallising the residue from toluene. The same compound is formed by boiling diazonitrophenyl perbromide with alcohol. It crystallises in long white needles, melting at 173°, and boiling above 360°. On oxidation it yields *parabromobenzoic acid* and a little *paranitrobenzoic acid*.

Isobromonitrodiphenyl.—This isomeride is formed, together with the preceding compound. It is readily soluble in alcohol, and forms fine crystals, melting at 65°, and boiling at about 360°. The same compound is also produced by treating isodiazonitrophenyl perbromide with alcohol.

Dinitrodiphenyl, $C^{12}H^4(NO^2)_2$, is best prepared by adding 6 pts. of concentrated nitric acid and 1 pt. of sulphuric acid to 3 pts. of diphenyl, and when the violent reaction is over, boiling the mixture for a short time. The crude product is exhausted with boiling alcohol to remove isodinitrodiphenyl. The pure compound crystallises in needles, melting at 233°, and not at 213°, as Fittig found (iv. 410). It is soluble in hot sulphuric acid, and crystallises again on cooling. A solution of chromic trioxide in glacial acetic acid does not oxidise it, and may be used for purification, the compound separating on the addition of water as a pure white precipitate. By the action of hydrogen sulphide it is reduced to *amidonitrodiphenyl*, $C^{12}H^4(NO^2)NH^2$, possessing all the properties of Fittig's compound, with the exception of the melting point, which was found to be 198°, instead of 160°. On oxidation it yields *paranitrobenzoic acid*. By passing nitrous acid into a mixture of amidonitrodiphenyl and hydrochloric acid cooled by snow, until all is dissolved, and then adding a mixture of bromine and hydrobromic acid, a perbromide is obtained as a dark red precipitate, which by boiling absolute alcohol, is converted into the bromonitrophenyl melting at 173°. Now as amidonitrodiphenyl yields *paranitrobenzoic acid*, and the corresponding bromonitrodiphenyl yields *parabromobenzoic acid*, it follows that all the *disubstitution-products* of diphenyl which are not distinguished by the prefix *iso*, are *dipara-* or *para-para-derivatives*.

When the action of the hydrogen sulphide is continued for some time, or assisted by heat, the (*p-p*) dinitrodiphenyl is reduced to a *diamidodiphenyl*, $C^8H^4(NH^2)-C^8H^4(NH^2)$, identical with benzidine (from azobenzene, i. 544), which is therefore also a (*p-p*) derivative.

Benzidine exhibits the following characteristic reactions:—potassium permanganate colours it blue; chromic acid converts it into a black body; and chlorine converts these, as well as benzidine, into a red substance having the appearance of ferric hydrate. It is insoluble in water and acids, and is converted into an acid by oxidising it with potassium dichromate and sulphuric acid.

Isodinitrodiphenyl may be obtained from the alcoholic mother-liquors of the preceding compound, and crystallises from alcohol in long colourless needles, melting at 93.5°. Like its isomeride, it may be purified with chromic acid, although it appears that some of it is completely oxidised by this treatment.

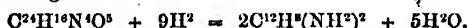
Isoamidonitrodiphenyl is produced by passing hydrogen sulphide into a mixture of the dinitro-compound, ammonium sulphide, and alcohol. It is almost insoluble in water, readily in alcohol, and crystallises in short red prisms melting at 97-98°. Its hydrochloride, $C^{12}H^9(NO^2)NH^2.ClH$, crystallises from hot water in long, white needles.

By reduction with tin and hydrochloric acid, isoamidonitrodiphenyl is converted into diphenylamine, $C^{12}H^9(NH^2)^2$.

The *perbromide of the diazo-compound of isoamidonitrodiphenyl*, yields by decomposition a bromonitrodiphenyl identical with that which is obtained as above from bromodiphenyl (m.p. 65°): consequently the amido-group in isoamidonitrodiphenyl occupies the para-position.

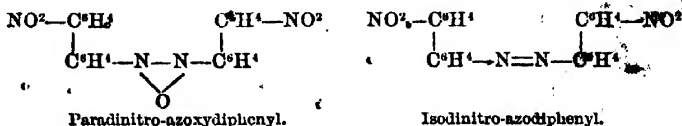
Dibromodinitrodiphenyl, $C^{12}H^8Br^2(NO^2)^2$, obtained by treating dibromodiphenyl with strong nitric acid, crystallises from benzene in needles melting at 148°. It is not attacked by chromic acid dissolved in glacial acetic acid, but is reduced by tin and hydrochloric acid to dibromodiamidodiphenyl, $C^{12}H^8Br^2(NH^2)^2$, which melts at 89°, and is converted by oxidation with chromic acid into an acid containing bromine and nitrogen, and melting at 155°.

AZO-DERIVATIVES OF DINITRODIPHENYL. H. Wald, *Deut. Chem. Ges. Ber.* x. 137).
1. *Paradinitroazoxydiphenyl*, $C^{12}H^{10}N^4O^3$.—This compound is formed by the action of sodium-amalgam on paradinitrodiphenyl suspended in alcohol, and is purified by washing it successively with alcohol, chloroform, and ether, in which it is nearly insoluble, dissolving it in boiling aniline; filtering; freeing the red powder which separates on cooling from mother-liquor by means of the filter-pump; and finally washing with alcohol and ether, and drying. It forms a brick-red crystalline powder, insoluble in most liquids, but readily soluble in boiling aniline. It melts at 225°, dissolves with fine deep red colour in strong sulphuric acid, and forms with strong nitric acid a yellow compound, insoluble in alcohol and ether, but soluble in benzene. By reduction with tin and hydrochloric acid, or with alcoholic ammonium sulphide at 115°, it yields benzidine melting at 122°:



2. *Isodinitro-azodiphenyl*, $C^{12}H^{10}N^4O^4$, is formed by the action of sodium-amalgam on isodinitrodiphenyl suspended in alcohol, and separates during the reaction in yellow flocks, which may be washed on a filter with cold alcohol, and further purified by crystallisation from boiling alcohol, which dissolves it but sparingly, and deposits it on cooling as a yellow powder. It dissolves easily in chloroform and benzene; melts at about 187°; and dissolves with brown-red colour in strong sulphuric acid.

The two compounds just described may be formulated as follows:



Dicyanodiphenyl, $C^{12}H^8N^2=C^6H^5(ON)^2.C^6H^5$, is prepared by heating a dry mixture of potassium diphenyl-disulphonate and potassium cyanide in a stream of dry carbon dioxide; the reaction does not however go on so regularly as in the case of the monocyano-compound (p. 660). Dicyanodiphenyl is insoluble in water, sparingly soluble in cold, easily in hot alcohol, and crystallises therefrom in rhombic groups of thin colourless needles. It melts at 234°, and sublimes without decomposition in shining serrated laminae (Döbner, *Liebig's Annalen*, clxxii. 102).

Dioxydiphenyl or **Diphenol**, $C^{12}H^{10}O^2=C^6H^5(OH)^2$. Of the numerous possible modifications of this compound, four are at present known, three being symmetrical, that is, having one hydroxyl in each phenyl-group, and the fourth unsymmetrical.

1. Griess, in 1864, obtained a diphenol by the action of water on nitrate of tetrazodiphenyl (iv. 412; v. 1055), and the same modification has been further examined by Lincke (*J. pr. Chem.* [2], viii. 43), who obtains it by fusing the potassium or sodium salt of phenolparasulphonic acid with a caustic alkali. When this potas-

sium salt is heated with at least twice its weight of potassium hydroxide and a little water, a rather brisk reaction takes place after a while, hydrogen being evolved, and the mass gradually assuming a yellowish-brown colour. As soon as it has acquired the consistence of a thick syrup, it is left to cool, dissolved in water, and acidulated with sulphuric acid, whereupon carbon dioxide and sulphur dioxide are evolved, and resinous products separate out. * The unfiltered liquid, freed from dissolved gases by boiling, is shaken up with ether, and the thickish oil which remains after distilling off the ether is distilled after drying. The portion which passes over below 300° consists mainly of phenol, and the crude diphenol which passes over above that temperature soon solidifies in the receiver to a crystalline mass. The quantity obtained is about 5 or 6 per cent. of the phenolparasulphonic acid employed; a larger quantity may be obtained by fusing sodium phenolparasulphonate with caustic soda. The product, purified by several recrystallisations from water, and sublimation in a stream of carbon dioxide, forms white feathery groups of crystals having a silky lustre.

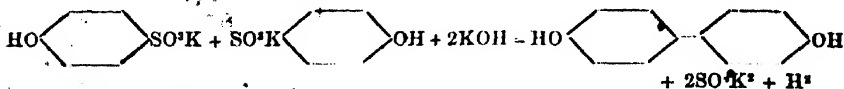
This diphenol crystallises from water in slender needles or rather broad prisms, which appear from approximate measurements by Siegart to belong to the orthorhombic system. Axial ratio:

Brachydiagonal. Macrodiagonal. Principal axis.

2.266	:	4.095	:	1
0.605	:	1	:	0.244

Combination, $\infty P : P : \infty P \infty : mP \infty$. Angle $\infty P : \infty P = 122^\circ 35'$; $P : P = 154^\circ 50'$. It melts at 156° – 158° , dissolves very sparingly in cold water, with difficulty in boiling water, easily in alcohol and ether. It dissolves also in alkalis, and is precipitated by acids. With *basic lead acetate* it forms a white precipitate. It is not reduced by passing its vapour over heated zinc-dust. With strong *nitric acid* it yields a nitro-product, the ammonia-salt of which crystallises in long needles. On pouring *bromine* into a solution of the diphenol in dilute alcohol, and heating the liquid in a water-bath, a flocculent substance separates, which crystallises from alcohol in microscopic needles. Strong *sulphuric acid* quickly dissolves the diphenol at the heat of the water-bath, forming a sulpho-acid, the aqueous solution of which dries up to friable masses.

This diphenol, being formed from 2 mols. of paraphenolsulphonic acid, $C_6H_4 \begin{smallmatrix} \text{OH} \\ \text{SO}_3H \end{smallmatrix}$ (1 : 4), is of symmetrical structure, and has its two hydroxyls in the para-position with respect to the point of junction, that is to say, it is dipara-diphenol:



2 and 3. These bodies are produced by fusing phenol with potassium hydroxide. Barth in 1870 (*Liebig's Annalen*, clvi. 93) obtained in this manner a yellowish-brown mass consisting of a diphenol, together with salicylic and oxybenzoic acids, the diphenol separated from it being a viscid oil, in which crystals formed after several weeks. This product has lately been further examined by Barth & Schreder (*Deut. Chem. Ges. Ber.* 1878, 1333). The crude product was distilled under a reduced pressure of 150 mm., the greater portion passing over between 310° and 330° . The distillate after a short time solidified to a hard crystalline mass, consisting of two kinds of crystals, namely, long needles and laminae. These were purified and separated by a long process of fractional crystallisation, &c., for the details of which reference must be made to the original paper. Both consist of diphenols (α and β), the acicular modification being by far the most abundant.

α -Diphenol crystallises in anhydrous slender flattened needles often more than 1 cm. long. It is more soluble in water than the β -compound, but nevertheless crystallises out first from the mixture of the two obtained as above, on account of its much larger quantity. It dissolves easily in alcohol, ether, chloroform, benzene, xylene, &c. Its aqueous solution forms with *ferric chloride* a liquid having a corn-flower-blue colour, which remains for weeks without alteration or turbidity, but is decolorised by sodium carbonate, and when heated deposits a red-brown precipitate, not however consisting of ferric oxide. It melts below 100° when immersed in water, and at 128° in the dry state. Vapour-density (obs.) = 6.40; (calc.) = 6.44.

α -Diphenol, distilled over *zinc dust*, yields a large quantity of diphenyl. Heated to 130° for some hours in a sealed tube with potash, methyl iodide, and a small quantity of methyl alcohol, it yields liquid dianisol.

α -Diphenol heated with a quantity of sulphuric acid slightly in excess of that which is required by the equation:



is converted into a diphenol-disulphonic acid, which may be obtained pure by evaporating the liquid in a platinum dish till fumes of sulphuric acid begin to escape, then neutralising the slight excess of sulphuric acid as nearly as possible with the calculated quantity of lead carbonate, freeing the filtrate from traces of dissolved lead by hydrogen sulphide, again filtering, and evaporating the liquid to a syrup; it then solidifies in the exsiccator to a light grey crystalline mass. Diphenoldisulphonic acid thus obtained is extremely soluble in water. Heated to 110° it decomposes, and is converted into a brown, varnish-like, extremely hygroscopic mass, which is also formed when the acid is subjected to prolonged drying at 100° in contact with the air. The sodium salt, $C^{12}H^8SO^4Na^2$, obtained by saturation, separates in stellate groups of slender needles containing 2 mols. water, which are given off at 200° . The potassium salt crystallises in needles with 1 mol. H^2O . The barium salt, obtained by decomposing the potassium or sodium salt with barium chloride, is a crystalline precipitate also containing water.

On heating the potassium salt of this disulphonic acid with excess of potash, acidulating the melt—whereupon it gives off sulphur dioxide—then digesting it with ether, evaporating off the ether, dissolving the residue in water, and leaving the solution to crystallise in a vacuum, a brownish crystalline mass is obtained consisting of matted needles, easily decomposable and very difficult to purify. Analysis gave 67.68 per cent. carbon and 4.78 hydrogen, whence, and from the mode of formation, it may be inferred that the substance is a tetroxydiphenyl, $C^{12}H^4(OH)^4$ (calc. 66.06 C. 4.59 H). By sublimation in a stream of hydrogen, a small quantity of this substance was obtained as a colourless crystalline film melting at 84° . Its aqueous solution gives with ferric chloride a light green colour reaction, changing, on addition of a very small quantity of dilute solution of sodium carbonate, to dark blue, on further addition to violet, and finally to red. This reaction, which is extremely delicate, is exactly the same as that exhibited by pyrocatechin, excepting that the green colour at first produced is somewhat lighter. The compound $C^{12}H^{10}O^2$ may therefore appropriately be called dipyrocatechin.

β -Diphenol, when pure, crystallises in small glittering laminae. It is somewhat sparingly soluble in water, and forms with ferric chloride a clear light green liquid, which, after a while, becomes turbid and colourless, and deposits green flocks. With other solvents it behaves like α -diphenol. It is anhydrous, melts at 190° , and at higher temperatures yields a vapour whose density is 6.39 (calc. 6.44). By distillation with *zinc* it yields a large quantity of diphenyl, and when treated with potash, methyl iodide, and a little methyl alcohol, it is converted into a crystalline dianisol.

These two diphenols, α and β , being formed from 2 mols. of phenol, have, like Griess's diphenol, a hydroxyl in each phenyl-group. Moreover as their formation is accompanied by that of a large proportion of salicylic and a small proportion of meta-oxybenzoic acid, but never by that of para-oxybenzoic acid, and as the proportion of α -diphenol produced is much greater than that of the β -modification, it is most probable that α -diphenyl is the di-*ortho*-modification, that is to say, has its two hydroxyls contiguous to the point of junction, and that β -diphenol is the di-*meta* or the *ortho-meta*-modification. It is, however, by no means impossible that one of the two may be an *o-m*-modification.

4. The fourth modification of diphenol was discovered in 1871 by Engelhardt & Latschinoff, who obtained it by the action of melting potash on the diphenyldisulphonic acid prepared by heating diphenyl with sulphuric acid (2nd Suppl. 938), and has been further examined by Doebner (*Deut. Chem. Ges. Ber.* ix. 129). As the reaction just mentioned does not take place very easily, it is best, after precipitating the resulting diphenol with an acid, to fuse it again with potash and reprecipitate. The diphenol thus prepared is sparingly soluble in water and benzene, dissolves easily in alcohol and ether, crystallises from alcohol in shining laminae, sublimes in fan-shaped groups of scales, and melts at 269° – 270° . It is energetically attacked by oxidising agents, and reduced by heating with zinc-dust to diphenyl. Fuming sulphuric acid converts it into a diphenyl-disulphonic acid, the potassium salt of which, $C^{12}H^4(OH)^2(SO^2K)^2$, forms prisms slightly soluble in water. On heating the diphenol with 2 mols. PCl^3 , dichlorodiphenyl, $C^{12}H^2Cl^2$, distils over as a white substance which gradually solidifies, and after repeated crystallisation from glacial acetic acid, forms geodes of small needles; it sublimes in long shining needles, and melts at 179° . It is insoluble in water, nearly insoluble in alcohol, ether, and benzene. When oxidised with chromic acid and glacial acid, it yields dichlorobenzoic acid

melting at 201° . Hence it follows that the diphenyl-disulphonic acid from which this dichloro-compound is derived, and all its other derivatives, are unsymmetrical bodies, having their two substituted radicles in the same phenyl-group. The diphenol is therefore represented by the formula $\text{C}^6\text{H}_4(\text{OH})_2 = \text{C}^6\text{H}_4$.

The four diphenols above described are sharply distinguished by their melting points, as shown by the following table:

<i>Symmetrical, $\text{C}^6\text{H}_4(\text{OH})_2 = \text{C}^6\text{H}_4$:</i>		Melting point
1. From phenolparasulphonic acid (Griess)	.	$156^{\circ} - 158^{\circ}$
2. From phenol (Barth a. Schreder) α	.	$269^{\circ} - 270^{\circ}$
3. " " " β	.	123°

<i>Unsymmetrical, $\text{C}^6\text{H}_3(\text{OH})_2 = \text{C}^6\text{H}_5$:</i>		
4. From diphenyl-disulphonic acid (Engelhardt a. Latschinoff, Doeblner)	.	190°

DIPHENYL-ACETALDEHYDE, $\text{C}^{12}\text{H}^{12}\text{O} = (\text{C}^6\text{H}_5)_2\text{CH} \cdot \text{COH}$. This compound is a thick, oily, colourless liquid, formed, together with solid products, by the action of dilute sulphuric acid upon hydrobenzoin or isohydrobenzoin, $\text{C}^{12}\text{H}^{12}\text{O}_2 = \text{H}^2\text{O} + \text{C}^{12}\text{H}^{12}\text{O}$. It volatilises with vapour of water, and is converted by oxidation into carbon dioxide and diphenylketone:



(Zincke a. Breuer, *Deut. Chem. Ges. Ber.* ix. 1769).

DIPHENYL-ACETIC ACID, $\text{C}^{12}\text{H}^{12}\text{O}_2 = (\text{C}^6\text{H}_5)_2\text{CH} \cdot \text{CO}^2\text{H}$ (Symons a. Zincke, *ibid.* vi. 1188). This acid, also called *deoxybenzic acid*, which Jena obtained by heating benzoic acid to 150° with concentrated hydriodic acid (*2nd Suppl.* 158), may be prepared synthetically by heating phenylbromacetic acid with benzene and zinc. The product of the somewhat violent reaction is a viscid colourless syrup, probably consisting of the fused zinc salt of diphenylacetic acid. By converting this salt into a barium salt and repeatedly crystallising the latter from alcohol, or, better, by preparing and crystallising the ethylic ether, the diphenylacetic acid may be obtained pure, and then exhibits all the properties of the acid described by Jena; so likewise does the *barium salt*, which separates from alcoholic solution in large, very efflorescent, monoclinic crystals containing 2 mols. combined alcohol. The *silver salt*, on the other

thick shining needles, which melt when heated under water. On recrystallising it from water, basic salts are very apt to form. The *ethylic ether*, $\text{C}^{12}\text{H}^{12}\text{O}_2 \cdot \text{C}^2\text{H}_5$, crystallises from alcohol in colourless, transparent, rectangular prisms with perpendicular end-faces; it dissolves easily in ether, alcohol, and carbon sulphide.

On treating synthetically prepared diphenylacetic acid with bromine-vapour at $140^{\circ} - 150^{\circ}$, and boiling the resinous product with water or barium hydrate, diphenylglycollic acid, $(\text{C}^6\text{H}_5)_2\text{COH} \cdot \text{CO}^2\text{H}$, is obtained, agreeing in all its properties with benzoic acid from benzil. This shows that benzoic acid has the structure assigned to it by Städeler (*2nd Suppl.* 158).

In the synthesis of diphenylacetic acid there is also formed a small quantity of a bibasic acid, $\text{C}^6\text{H}_4[\text{CH}(\text{C}^6\text{H}_5)_2 \cdot \text{CO}^2\text{H}]_2$, which separates from its barium salt on addition of hydrochloric acid in yellow resinous drops, which gradually solidify and then melt at 110° ; it cannot be crystallised. The barium salt is insoluble in alcohol.

DIPHENYLAMINE. See PHENYLAMINES.

DIPHENYL-ARSENIOUS CHLORIDE, $(\text{C}^6\text{H}_5)_2\text{AsCl}$. See PHENYL-ARSENIC COMPOUNDS.

DIPHENYL-BENZENE, $\text{C}^{12}\text{H}^{10} = \text{C}^6\text{H}_4(\text{C}^6\text{H}_5)_2$. Two modifications of this compound are formed, together with diphenyl and other products, by passing benzene vapour through a red-hot tube. On rectifying the crude product, the two diphenyl-benzenes pass over after the diphenyl, and may be separated from one another by repeated crystallisation from alcohol, in which one is freely, the other sparingly soluble.

Paradiphenyl-benzene, the less soluble modification, constitutes the chief part of the product designated by Berthelot as *benzerythrene* (*1st Suppl.* 304), and is identical with the hydrocarbon which Riese obtained by the action of sodium on an

666 DIPHENYL-BENZHYDRYL—DIPHENYL CARBINOL.

ethereal solution of solid dibromobenzene and monobromobenzene (*2nd Suppl.* 945). It is also formed, together with ethylene, by the action of ethyl bromide on potassium-benzene (p. 160). It melts at 205°, boils above 360°, and has a vapour-density = 8.43 (calc. 8.05). Near its melting point it sublimes in iridescent laminae. It is insoluble in water, dissolves but sparingly in alcohol even at the boiling heat, more easily in ether, carbon sulphide, and light petroleum, and with moderate facility in benzene, especially when warm. It does not appear to combine with picric acid. By oxidation it yields first paradiphenyl-carbonic acid, $C^6H^4-C^6H^4(CO^2H)$, and then terephthalic acid (G. Schultz, *Deut. Chem. Ges. Ber.* vi. 415; *Liebig's Annalen*, clxxii. 281; clxxiv. 230).

According to E. Schmidt (*Deut. Chem. Ges. Ber.* vii. 1865), paradiphenyl-benzene dissolved in carbon sulphide is not perceptibly attacked by bromine; but when treated with bromine under water, it yields a body crystallising in needles, the analysis of which gives numbers intermediate between those required by a tri- and a tetra-brominated derivative.

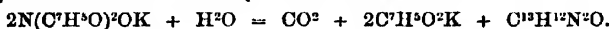
Isodiphenylbenzene, the modification easily soluble in alcohol, dissolves easily also in ether, benzene, and glacial acetic acid, but is insoluble in water. From dilute alcoholic solution it crystallises in stellate groups of long white needles, melting at 86°. It boils at about 360°, and has a vapour-density = 8.29. It does not unite with picric acid. By oxidation with chromic acid in glacial acetic acid solution, it yields benzoic acid (Schultz, *loc. cit.*)

DIPHENYL - BENZHYDRYL, $C^{20}H^{20}O = C^{12}H^{10}(C^6H^5)_2O = C^6H^4(C^6H^5)-CHOH-C^6H^4(C^6H^5)$, is formed by the action of sodium-amalgam on diphenyl-benzophenone. It crystallises in small white needles melting at 226° (uncorr.), and dissolves with extraordinary facility in alcohol and benzene (Weiler, *Deut. Chem. Ges. Ber.* vii. 1188).

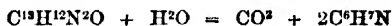
DIPHENYL-BENZOPHENONE. See PHENYL-KETONES.

DIPHENYL-CARBAMIC CHLORIDE, $CO \begin{smallmatrix} \text{Cl} \\ \text{N} \end{smallmatrix} (C^6H^5)_2$, is formed by the action of carbonyl chloride on diphenylamine dissolved in chloroform (p. 391).

DIPHENYL-CARBAMIDE, $C^{12}H^{12}N^2O$. The symmetrical modification of this compound, $NH(C^6H^5).CO.NH(C^6H^5)$ (p. 390), is formed by the action of water on the potassium salt of dibenzhydroxamic acid (*2nd Suppl.* 155):



It does not unite with acids or with alkalis, but when heated to 180° for several hours with strong hydrochloric acid, it is resolved, with assumption of water, into CO^2 and aniline:

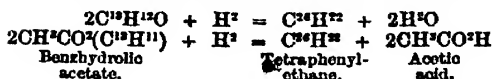


(Losseh, *Deut. Chem. Ges. Ber.* vi. 1392).

DIPHENYL-CARBINOL, $C^{12}H^{12}O = C^6H^5-CHOH-C^6H^5$. *Benzhydrol*.—This body, first obtained in 1865 by Linnemann, who prepared it by the action of sodium-amalgam on an alcoholic solution of benzophenone or diphenyl ketone (iv. 478), is likewise produced when the same ketone (3 pts.) is heated with alcoholic potash (1 pt. KHO in 5 pts. alcohol of 95 per cent.) to 160° in sealed tubes for five hours. The contents of the tubes when cold are washed out with a little hot water, and the resinous residuum is boiled with water as long as the filtrate continues to yield crystals: the yield amounts to 75 per cent. of the benzophenone. A still larger amount is obtained by dissolving benzophenone in potash-ley and boiling the solution with zinc. Diphenyl-carbinol is also produced by heating benzophenone for five hours to 180° with an alkaline solution of amyl alcohol; no resin is then separated, but valerianic acid is produced at the same time (Zagoumeny, *Liebig's Annalen*, clxxiv. 174).

Diphenyl-carbinol is not altered by prolonged heating with strong alcoholic solutions of alkalis even at 180°–200° in sealed tubes; but when heated to 180° in a sealed tube with sulphuric acid diluted with 5 vols. water, it is converted into the benzhydrol ether, $C^{20}H^{20}O = 2C^{12}H^{12}O - H^2O$, which Linnemann obtained by simply heating the alcohol, or by treating it with chloride or iodide of phosphorus (iv. 478).

Diphenyl-carbinol is not attacked by zinc when it is dissolved in glacial acetic acid, or by hydrochloric acid and zinc when it is dissolved in alcohol; but the action of strong aqueous hydrochloric acid and zinc on diphenyl-carbinol dissolved in glacial acetic acid, gives rise to a hydrocarbon melting at 209°, which, according to Zagoumeny's analysis, has the composition of tetraphenylethane, $C^{20}H^{20} = C^6H^5(C^6H^5)^3$. Its formation may be represented by the following equations:



This hydrocarbon dissolves in 128 pts. of boiling alcohol of 95 per cent., in 21 pts. of boiling acetic acid, in 7 pts. of boiling benzene, and crystallises from the alcoholic and acetic solutions in slender needles, from benzene in transparent bulky rhombic prisms (a compound of 1 mol. tetraphenylethane with 1 mol. benzene). It appears to be identical with the hydrocarbon (formulated as $\text{C}^{12}\text{H}^{10}$) which Linnemann obtained by distillation of the benzoic and succinic ethers of diphenyl-carbinol (iv. 475).

DIPHENYL-CARBONIC or **PHENYL-BENZOIC ACID**, $\text{C}^{12}\text{H}^{10}\text{O}^2 = \text{C}^6\text{H}^5.\text{C}^6\text{H}^4.\text{CO}^2\text{H}$. Two modifications of this acid are known. One, obtained by the action of melting potash on diphenylene ketone,



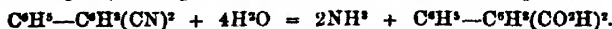
dissolves sparingly in cold water, with moderate facility in hot water, very easily in alcohol, and melts at $102^\circ\text{--}103^\circ$ (Fittig & Ostermeyer, *Deut. Chem. Ges. Ber.* v. 933). It is not known whether the phenyl-group in this acid is in the ortho- or the meta-position with regard to the group CO^2H .

Paradiphenyl - carbonic or **Paraphenyl - benzoic acid**, $\text{C}^6\text{H}_4.\text{H}.\text{C}^6\text{H}_4.\text{CO}^2\text{H}$, is produced: 1. By oxidation of diphenyl-benzene. This compound, dissolved in glacial acetic acid, is heated with five times its weight of chromic acid; the solution is precipitated by water; the precipitate, consisting of unaltered diphenylbenzene and the acid, is digested with ammonia which extracts the latter; and the filtrate is precipitated with hydrochloric acid (Schultz, *ibid.* vi. 417). 2. By boiling cyanodiphenyl, $\text{C}^{12}\text{H}_8.\text{CN}$, with alcoholic potash. In this process, a sparingly soluble substance, evidently the amide of the acid, separates at first, but disappears on prolonged boiling (Doebner, *Liebig's Annalen*, clxxii. 109). 3. By oxidation of para-tolylphenyl, $\text{CH}^3.\text{C}^6\text{H}_4.\text{C}^6\text{H}_5$ (Carnelley, *Chem. Soc. Jour.* 1876, i. 19).

Paradiphenyl-carbonic acid crystallises in tufts of needles, melts at $216^\circ\text{--}217^\circ$ (Schultz), at $218^\circ\text{--}219^\circ$ (Doebner), and sublimes easily, somewhat above its melting point, in long needles. It is slightly soluble in water, more easily in alcohol and ether. The ammonium salt crystallises in tufts of laminae. The barium salt, $(\text{C}^{12}\text{H}^{10}\text{O}^2)^2\text{Ba}$, is precipitated by barium chloride from the solution of the ammonium salt, as a granulo-crystalline, nearly insoluble precipitate. From a hot saturated solution it crystallises on cooling in thin shining plates. The calcium salt is prepared like the barium salt, and resembles it in every respect. The magnesium salt may be obtained by precipitation, or by saturating the acid with magnesium carbonate, in which case it often separates in nodular groups of laminae. Like the preceding salts it is anhydrous after drying over sulphuric acid. Most of the other diphenyl-carbonates are insoluble or sparingly soluble. In neutral solutions of the ammonium salt, zinc sulphate produces a white granular precipitate; cupric sulphate a blue-green; ferric sulphate a yellow; lead nitrate and silver nitrate white precipitates. The ethylic ether, $\text{C}^{12}\text{H}^8.\text{CO}^2\text{C}^2\text{H}_5$, prepared by means of alcohol and hydrochloric acid gas, forms large colourless prisms melting at 46° , easily soluble in alcohol (Doebner).

Paradiphenyl-carbonic acid, heated with calcium hydrate, is resolved into carbon dioxide and diphenyl, $\text{C}^{12}\text{H}_8.\text{CO}^2\text{H} = \text{CO}^2 + \text{C}^{12}\text{H}^{10}$. By oxidation with chromic acid in glacial acetic solution, it yields terephthalic acid (Schultz).

DIPHENYL-DICARBONIC ACID, $\text{C}^{12}\text{H}^{10}\text{O}^4 = \text{C}^6\text{H}^5\text{—C}^6\text{H}^4(\text{CO}^2\text{H})^2$ (Doebner, *loc. cit.*; also *Deut. Chem. Ges. Ber.* ix. 2, 129). This acid, metameric with diphenic acid (p. 668), is formed by boiling dicyanodiphenyl derived from unsymmetrical diphenyl-disulphonic acid (p. 665), with alcoholic potash:



The conversion is, however, much more difficult than that of cyanodiphenyl into diphenyl-monocarbonic acid, a large portion of the cyanogen-compound being converted into a white powder perfectly insoluble in all the ordinary solvents, doubtless the diamide of the dicarbonic acid. But even the acid obtained from the filtrate is not pure, but appears to contain the monamide or amidic acid, $\text{C}^{12}\text{H}^8\text{—C}^6\text{H}_4\begin{smallmatrix} \text{CONH}^2 \\ \text{COOH} \end{smallmatrix}$, the complete conversion of which into the dicarbonic acid can be effected only by repeated evaporation of the crude acid mixed with a large excess of caustic potash. A better method of effecting the decomposition of the dicyanodiphenyl is to heat it to 180° for

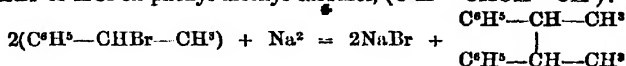
twelve hours with strong hydrochloric acid. Diphenyl-dicarbonic acid is also produced by oxidation of ditolyl dissolved in glacial acetic acid with chromic acid.

Pure diphenyl-dicarbonic acid is a white amorphous powder deceptively like terephthalic acid, and, like the latter, nearly insoluble in all the ordinary solvents. It neither melts nor sublimates, and requires a very high temperature to decompose it. Its salts, except those of the alkalis, are nearly all insoluble in water. The *barium* and *calcium* salts are white precipitates, nearly insoluble in water, even at the boiling heat; anhydrous after drying over sulphuric acid. The *silver* salt, $C^{10}H^8O^4Ag^2$, is a white precipitate, which cakes together in water, and is somewhat soluble therein. In the dilute solution of the ammonium salt, *magnesium sulphate* produces no precipitate, *zinc sulphate* and *lead nitrate* form white precipitates, *cupric sulphate* a bluish white, *ferric chloride* a light yellow precipitate. The *ethylac*, which can be prepared only by decomposing the silver salt with ethyl iodide, forms large flat prisms slightly soluble in cold, easily in boiling alcohol, melting at 112° .

Diphenyl-dicarbonic acid, heated with excess of lime, is decomposed like the monocarbonic acid, yielding diphenyl. It cannot be oxidised by chromic acid, on account of its insolubility in glacial acetic acid (Doebner, *loc. cit.*)

DIPHENYL-DIMETHYL-ETHANE, $C^{10}H^{12}$ = $\begin{array}{c} C^6H^5-CH-CH^3 \\ | \\ C^6H^5-CH-CH^3 \end{array}$ (Hengler

a. Bethge, *Deut. Chem. Ges. Ber.* vii. 1127). This hydrocarbon is formed by the action of sodium on secondary phenyl-methyl-carbinyl bromide or chloride (produced by the action of HBr or HCl on phenyl-methyl carbinol, $(C^6H^5-CHOH-CH^3)$):



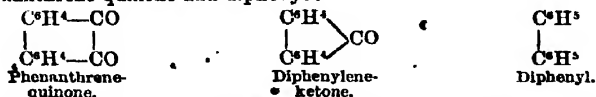
In either case a mixture of liquid and solid products is obtained, from which, by filtration and recrystallisation of the solid portion from alcohol, the diphenyl-dimethyl-ethane may be isolated. It crystallises in colourless needles, melts at 123.5° , and sublimates without decomposition.

DIPHENYLENE-COMPOUNDS. A comparison of the boiling points of corresponding diphenyl and diphenylene compounds—the latter containing 2 at. hydrogen less than the former, and having the two phenylene-groups directly united—shows that the diphenylene-compounds boil at temperatures about 40° higher than the corresponding diphenyl-compounds, in which the two phenyl-groups are not directly united. This is shown by the following table:

		Boiling point
Diphenyl oxide	$(C^6H^5)^2O$	246°
Diphenylene oxide	$(H^4C^6-C^6H^4)O$	$287^\circ-288^\circ$
Diphenyl-methane	$(C^6H^5)^2CH^2$	$261^\circ-262^\circ$
Diphenylene-methane	$(H^4C^6-C^6H^4)CH^2$	$300^\circ-304^\circ$
Diphenyl sulphide	$(C^6H^5)^2S$	292.5°
Diphenylene sulphide	$(H^4C^6-C^6H^4)S$	$332^\circ-333^\circ$
Diphenyl ketone	$(C^6H^5)^2CO$	295°
Diphenylene ketone	$(H^4C^6-C^6H^4)CO$	$336^\circ-338^\circ$
Stilbene	$(C^6H^5)^2C^2H^2$	$306^\circ-307^\circ$
Phenanthrene	$(H^4C^6-C^6H^4)C^2H^2$	340°
Diphenylamine	$(C^6H^5)^2NH$	310°
Carbazole	$(H^4C^6-C^6H^4)NH$	364°

The law exhibited by these numbers may serve in some cases to determine the decision in favour of a particular formula, or to estimate approximately the boiling point of any member of either series when that of the corresponding compound in the other series is known (Graebe, *Deut. Chem. Ges. Ber.* vii. 1629).

Diphenylene Ketone, $C^{18}H^{12}O$. This compound is intermediate in composition between phenanthrene-quinone and diphenyl:



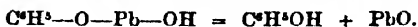
It is the chief product obtained by distilling phenanthrene quinone with quick lime (Anschütz a. Schultz, *Deut. Chem. Ges. Ber.* ix. 1400).

Diphenylene Oxide, $\begin{array}{c} C^6H^4 \\ | \\ C^6H^4 \end{array} O$. This compound, discovered by Lesimple, who

regarded it as phenyl oxide, and further examined by Hoffmeister, who determined its true composition (2nd Suppl. 436), may be prepared by heating the lead-compound of phenol:



This process, however, yields but a small quantity of diphenylene oxide (from 3 to 4 per cent. of the phenol-compound used), while a large quantity of phenol is at the same time regenerated, probably because the phenol and lead oxide chiefly unite to form a basic compound, which is then decomposed by heat, according to the equation



A better method is to heat in a capacious retort, 1 pt. of phenol with 1 to 1½ pts. lead oxide. Phenol then distils over first, after which the contents of the retort froth up and turn grey, dark violet, and finally black, whereupon a mixture of phenol and diphenylene oxide distils over and solidifies to a red crystalline mass. The two compounds are separated by soda-ley, the crude diphenylene oxide is distilled over, and the portion which distils below 300° is crystallised from alcohol. It melts at 80°–81°, boils at 287°–288°, and has a vapour-density = 5.97 (Graebe, *Liebigs Annalen*, clxxiv. 190).

As bye-product in the above reaction, there is obtained a body which boils at a higher temperature than diphenylene oxide, melts at about 170° and dissolves easily in alcohol (Graebe).

Behr a. van Dorp (*Deut. Chem. Ges. Ber.* vii. 398), by gently heating phenol with five or six times its weight of lead oxide, have also obtained diphenylene oxide, together with unaltered phenol, and a body having the composition $\text{C}^{12}\text{H}^8\text{O}^2$. The crude dis-

lising in laminae, and the compound $\text{C}^{12}\text{H}^8\text{O}^2$ in needles. The two are separated by distillation with steam, in which only the diphenylene oxide volatilises readily. The compound $\text{C}^{12}\text{H}^8\text{O}^2$ (doubtless identical with the bye-product mentioned by Graebe) is insoluble in alkalis, dissolves easily in benzene and in alcohol, less easily in light petroleum, and melts at 173°–174°. Triturated with bromine and water, it yields the compound $\text{C}^{12}\text{H}^6\text{Br}^2\text{O}^2$ which crystallises from alcohol in needles melting at 211°–212°.

Diphenylene Sulphides (Graebe, *Liebigs Annalen*, clxxiv. 185). 1. *Mono-*

sulphide, $\text{C}^{12}\text{H}^8\text{S} = \begin{array}{c} \text{C}^6\text{H}^5 \\ \text{C}^6\text{H}^5 \end{array} \text{S}$. Stenhouse obtained this compound by passing the

vapour of phenyl sulphide, $\text{C}^6\text{H}^5\text{S}$, through a red-hot tube filled with iron nails; but he regarded it as an isomeric modification of phenyl sulphide, and called it *paraphenyl sulphide* (2nd Suppl. 941). Graebe, however, finds that it contains 2 atoms of hydrogen less. He prepares it by passing the vapour of phenyl sulphide through a red-hot combustion-tube—whereby benzene, hydrogen, hydrogen sulphide, and apparently also free sulphur, are formed at the same time,—and fractionating the product. The fraction 295°–330° solidifies partially on cooling, and a further quantity of this solid product is obtained by pipetting off the liquid portion, again passing its vapour, together with that of the lower-boiling portions, through the red-hot tube, and repeating these operations several times.

Diphenylene sulphide crystallises from alcohol in long silky needles, from weak spirit sometimes also in laminae. It melts at 97°, and boils at 332°–333° (mercury-column wholly in the vapour). It is moderately soluble in cold alcohol, very soluble in hot alcohol and in ether, soluble also in benzene. It is not altered by heating to 260°–280° with strong hydriodic acid and phosphorus. By oxidation with chromic acid mixture it yields Stenhouse's *parasulphobenzide*, to which he assigned the formula $\text{C}^{12}\text{H}^{10}\text{SO}^2$ (2nd Suppl. 941). According to Graebe, however, this compound contains 2 at. hydrogen less, and consists of diphenylenesulphone or diphenylene

oxysulphide, $\text{C}^{12}\text{H}^8\text{SO}^2 = \begin{array}{c} \text{C}^6\text{H}^5 \\ \text{C}^6\text{H}^5 \end{array} \text{SO}^2$. With regard to its properties, Graebe corroborates the statements of Stenhouse.

The disulphide, $\text{C}^{12}\text{H}^8\text{S}^2$ (Stenhouse's *phenylene sulphide*, 1st Suppl. 922), is formed in the preparation of phenyl sulphide and hydrosulphide by the action of phosphorus pentasulphide on phenol. When 2 pts. of phenol are heated with 1 pt. of phosphorus pentasulphide, a brisk reaction occurs, sulphuretted hydrogen escapes, and a distillate, consisting essentially of phenol and phenyl hydrosulphide passes over. At a higher temperature the chief products obtained are benzene, phenyl

sulphide, and crystals of diphenylene disulphide. On rectification of the product, crystals separate on cooling from all portions which pass over above 290° – 295° . These crystals must be purified by washing with cold alcohol and recrystallisation from benzene or hot alcohol. The composition of the body thus prepared is C^6H^4S , but its vapour-density shows that the formula must be doubled— $C^{12}H^8S^2$.

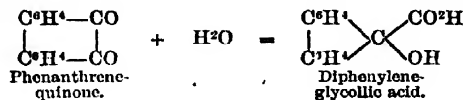
Diphenylene disulphide crystallises in colourless brilliant prisms, melts at 154° – 155° , sublimes in needles, and boils at about 363° . It is insoluble in water, slightly soluble in cold alcohol, but dissolves moderately well in boiling alcohol; benzene, ether, and carbon disulphide dissolve it in the cold, but it is taken up in largest quantity by boiling benzene. It dissolves also in cold concentrated sulphuric acid, but more quickly and with production of an intense violet colour when heated. From this solution water precipitates unaltered diphenylene disulphide. When the solution in sulphuric acid is strongly heated, the violet colour changes to brown, and water no longer produces a precipitate.

From its behaviour to oxidising and reducing agents, diphenylene disulphide appears to have the constitution represented by the formula $C^6H^4 \begin{smallmatrix} \diagup S \diagdown \\ \diagdown S \diagup \end{smallmatrix} C^6H^4$, analo-

gous to that of azophenylene, $C^6H^4 \begin{smallmatrix} N \\ \diagdown \diagup \end{smallmatrix} C^6H^4$. With reducing agents it behaves like phenyl monosulphide, not like the disulphide. It is not attacked by zinc and hydrochloric acid, or by sodium-amalgam; and when heated to 200° with hydriodic acid and phosphorus, it emits only a faint odour, indicating the formation of a very small quantity of phenyl mercaptan.

Diphenylene-disulphone, $C^{12}H^8S^2O^4 = C^6H^4 \begin{smallmatrix} SO^2 \\ \diagdown \diagup \\ SO^2 \end{smallmatrix} C^6H^4$, is prepared from diphenylene disulphide, either by boiling with potassium dichromate and dilute sulphuric acid, or by oxidation with chromic acid dissolved in glacial acetic acid. The solution on cooling deposits the disulphone free from disulphide in nearly theoretical quantity. It is best purified by crystallisation from boiling benzene. When perfectly pure it gives no coloration on warming with concentrated sulphuric acid. It crystallises in colourless prisms or tables, is almost insoluble in alcohol and ether, slightly soluble in cold acetic acid and benzene, abundantly so on warming. Its melting point is above 300° , and it can be sublimed and distilled without alteration. It is indifferent towards acids and bases, but is decomposed by heating with soda-lime, yielding chiefly benzene mixed with a little diphenyl (Graebe, *Liebig's Annalen*, clxxix. 178).

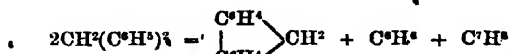
DIPHENYLENE-GLYCOLLIC ACID, $C^{14}H^{10}O^3$ (Friedlander, *Deut. Chem. Ges. Ber.* x. 125). An acid formed by the action of alkalis on phenanthrene-quinone, probably as follows:



When phenanthrenequinone is heated with soda-ley, it turns brown and yields a brown solution which becomes colourless after prolonged boiling, and on addition of

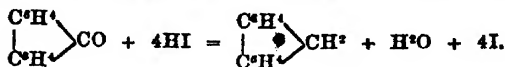
with a faint indigo-blue colour, which disappears on addition of water; easily also in alkalis; and is precipitated unchanged by acids. The calcium salt, $(C^6H^4O^2)^2Ca$, forms colourless slightly soluble crystals.

DIPHENYLENE-METHANE or *Methylene-diphenyl*, $C^{12}H^{10} = \begin{smallmatrix} C^6H^4 \\ | \\ C^6H^4 \end{smallmatrix} CH^2$ (Graebe, *Liebig's Annalen*, clxxxiv. 194). This compound is formed, together with benzene and toluene, by passing the vapour of diphenyl-methane through a red-hot tube:



The quantity of diphenylene-methane thus obtained is but small, and therefore the purification is difficult. On fractionating the crude product, a mixture of diphenylene-methane, diphenyl-methane, and higher-melting bodies passes over between 295° and 310° , while a proportionately large quantity of high-boiling products remains in the retort. Diphenylene-methane is also produced by reduction of diphenylene

ketone with heated zinc-dust (2nd Suppl. 946), or with hydriodic acid and amorphous phosphorus :



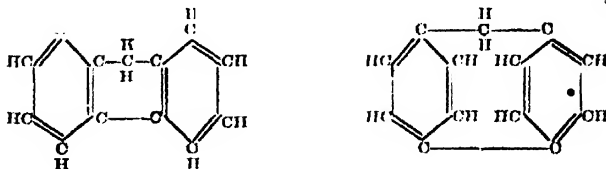
It is isomeric with fluorene (*infra*).

Diphenylene-methane crystallises in colourless laminae which often exhibit a blue fluorescence. It melts at 113° – 114° , boils at 300° – 305° , and volatilises easily with vapour of water; dissolves easily in hot, less easily in cold alcohol, very easily in carbon sulphide, ether, and benzene. Its compound with picric acid crystallises from benzene in yellow-red or red needles, which melt at about 80° – 82° , and dissolve very easily in alcohol, but decompose at the same time.

Diphenylene-methane is oxidised with difficulty, yielding diphenylene ketone, $(\text{C}^6\text{H}_5)_2\text{CO}$.

Dibromodiphenylene-methane, $\text{C}^{12}\text{H}_8\text{Br}_2$, produced by trituration of the hydrocarbon with bromine and water, crystallises in needles and melts at 153° – 154° . It dissolves very sparingly in alcohol, abundantly in ether and benzene, very easily in carbon sulphide and chloroform.

Fluorene, $\text{C}^{14}\text{H}_{10}$. This hydrocarbon, isomeric or perhaps identical with the diphenylene-methane just described, was discovered in 1867 by Berthelot in the portion of coal-tar oil which boils between 300° and 340° (2nd Suppl. 523). It agrees with Graebe's diphenylene-methane in melting and boiling point, in the colour and melting point of its picric acid compound, and in the characters of the ketone, $\text{C}^{12}\text{H}_8\text{CO}$, which it yields by oxidation; but it likewise yields, by further oxidation with chromic acid mixture, a quinone, $\text{C}^{12}\text{H}_6\text{O}_2$, which does not appear to have been obtained from Graebe's diphenylene-methane (possibly because the oxidation was not carried far enough); and the dibromo-derivatives, $\text{C}^{12}\text{H}_8\text{Br}_2$, obtained from the two hydrocarbons, differ considerably in crystalline form and in melting point. The existence of two or more modifications of the hydrocarbon, $\text{CH}_2(\text{C}^6\text{H}_5)_2$, is indeed to be expected, the differences being attributable to the manner in which the two phenylene groups are linked together by the CH_2 -group. Two possible modifications are represented by the following formulae :



The properties of fluorene and its derivatives have lately been carefully examined by Barbier (*Ann. Chim. Phys.* [5], vii. 472). It is best prepared from the heavy oils from which anthracene and naphthalene have been separated, by first submitting them to fractional distillation, and collecting the portion passing at 290° – 340° (the distillate at 270° – 290° contains much acenaphthene); by a further series of fractionations a portion passing at 300° – 320° is isolated. To obtain a good result enough oil should have been originally employed to allow of 15 or 20 liters of this distillate being collected. By the action of cold, this fraction becomes nearly solid; the mass is pump-filtered, and the solid residue pressed in blotting paper, and then again distilled, collecting what passes at 290° – 310° . Above this temperature little but phenanthrene passes over, this hydrocarbon being thus obtained almost pure, and constituting about one-half of the pressed crystals. On again distilling and collecting at 295° – 305° , a yellowish-white mass is obtained, consisting of fluorene mixed with a little oxidised substance and some acenaphthene; these are eliminated by successively crystallising from a mixture of benzene and alcohol, alcohol alone, and glacial acetic acid. The last named solvent removes the oxidised substance, but the same result may also be obtained by exposing to sunlight a solution of the crude fluorene in benzene.

Absolutely pure fluorene may be prepared from the nearly pure substance thus obtained by dissolving it in ether, and adding the requisite quantity of picric acid. On slow evaporation fine red needles of the picric acid compound of the hydrocarbon separate, melting at 80° – 82° ; by treating these with ammonia, the hydrocarbon is set

free; and by repeating the combination with picric acid and regeneration several times, a perfectly pure product is obtained.

Fluorene thus prepared melts at 113° , boils at about 305° , and sublimes with some difficulty in granular aggregates of very small white plates, exhibiting a beautiful violet fluorescence, which, however, disappears on exposure to light. It is very soluble in ether, benzene, carbon sulphide, and hot alcohol, sparingly soluble in cold alcohol (Barbier). It unites with *picryl chloride*, forming the compound $C^{10}H^{14}.C^6H^3(NO_2)_3Cl$, which crystallises in orange-yellow needles melting at 69° – 70° (Liebermann a. Palm, *Ber.* viii. 377).

When fluorene is heated to about 275° with ten times its weight of a solution of *hydriodic acid* saturated at 0° , carbon is set free, together with various hydrocarbons of less complex character than fluorene, viz. benzene and toluene, together with a hydrocarbon boiling near 220° , and entirely soluble in fuming nitric acid. If a larger quantity of hydriodic acid be used (40 pts.) hexane and heptane and a tridecane, $C^{13}H^{26}$, are formed, together with a minute quantity of a hydrocarbon volatile at about 360° . The tridecane thus produced is not attacked either by nitric acid, cold bromine, or fuming sulphuric acid; it is also formed by heating fluorene to 200° with red phosphorus and hydriodic acid of sp. gr. 1.5.

Fluorene is slowly oxidised by *chromic acid* dissolved in glacial acetic acid, or by a mixture of potassium dichromate and sulphuric acid, forming diphenylene ketone, $C^{11}H^8O = (C^6H^4)_2CO$, and fluorenequinone, $C^{13}H^8O_2$, perhaps $CO < \begin{smallmatrix} C^6H^4 \\ C^6H^4 \end{smallmatrix} > O$, together with formic, oxalic, and phthalic acids. The ketone and quinone are insoluble in water, and may be separated from one another by means of a warm mixture of alcohol and benzene, which on cooling deposits grains of the quinone, while the ketone remains in solution. By recrystallising these grains from benzene the fluorene-quinone is obtained pure. It melts at 181° – 182° , is reduced to fluorene by heating it to 180° with iodine and phosphorus, and converted by sulphurous acid solution at 100° into a crystalline product probably consisting of fluorene-hydroquinone (Barbier).

When fluorene is distilled over moderately heated *lead oxide*, a semi-solid reddish product is obtained, which may be freed from resinous bodies by digestion with hot alcohol; and on dissolving the residue in a mixture of alcohol and benzene, the solution after a while deposits long yellow needles, which, after one recrystallisation, melt at 270° , and have the composition $nC^{11}H^7$. On evaporating the mother-liquor, and repeatedly boiling the residue with quantities of glacial acetic acid not sufficient to dissolve it, further quantities of this body are removed, and another hydrocarbon remains, which, when purified by recrystallisation from glacial acetic acid, forms large red well-defined shining crystals. This body has the composition $nC^{13}H^8$, melts at 182° – 183° and boils above 360° . It unites with *picric acid* in alcoholic solution, forming an unstable compound, $C^{26}H^{18}.C^6H^3N^3O^7$, which melts at 177° – 178° . When the vapour of this hydrocarbon is passed over heated *zinc-dust*, fluorene is formed together with other products. On treating this same hydrocarbon in boiling alcoholic solution with *sodium-amalgam*, the reddish liquid gradually becomes colourless, and yields a new hydrocarbon, $C^{26}H^{18}$, which crystallises from a mixture of benzene and alcohol in colourless needles melting at 241° – 242° . From the formation of this last hydrocarbon, and the composition of the above-mentioned picric acid compound, it may be inferred that the hydrocarbon melting at 182° – 183° has the composition $C^{26}H^{18}$, and that it is formed from fluorene in the manner shown by the equation:



Besides the hydrocarbons above mentioned, the action of heated lead oxide on fluorene gives rise to a body melting at 170° (C. de la Harpe a. W. A. van Dorp, *Dout. Chem. Ges. Ber.* viii. 1048).

Bromofluorenes. *Dibromofluorene*, $C^{11}H^6Br^2$, is obtained by adding the calculated quantity of bromine dissolved in carbon disulphide to a solution of fluorene in the same liquid. On distillation a residue is left, which may be freed from a red bye-product by washing with ether; the insoluble substance is then crystallised twice from carbon disulphide by spontaneous evaporation.

The crystals of dibromofluorene are monoclinic, and exhibit the combination $\infty P. 0P. \infty R \infty. \infty R 2. -P.$ Angle $\infty P : \infty P = 97^{\circ} 40'$; $0P : \infty P = 97^{\circ} 58'$; $0P : \infty R \infty = 102^{\circ} 10'$; $-P : 0P = 131^{\circ}$; $\infty R 2 : 0P = 94^{\circ} 55'$; $\infty R 2 : \infty R 2 = 132^{\circ} 42'$. Cleavage parallel to $0P$.

Dibromofluorene is nearly insoluble in ether and in alcohol, but dissolves readily in carbon sulphide and in chloroform. It melts at 166° – 167° , distils unchanged at a

high temperature, and is not attacked by boiling alcoholic potash. Heated with red-hot lime it yields diphenyl; and when treated with dinitroanthraquinone (Fritzsche's reagent), it forms lemon-yellow rhomboidal plates.

Tribromofluorene, $C^{10}H^7Br^3$, is formed by treating fluorene with excess of bromine, or by heating dibromofluorene with bromine:



but it is not easily obtained free from dibromofluorene, as the two compounds are almost equally soluble in carbon disulphide and in chloroform. The tribromo-derivative is insoluble in alcohol and in ether. After repeated crystallisation from carbon disulphide it forms light yellow needles, melting at 161° – 162° , and decomposing at a higher temperature.

Tetrabromofluorene, $C^{10}H^6Br^4$, resembles the tribromo-compound.

Monobromofluorene dibromide, $C^{10}H^7Br.Br^2 = \begin{smallmatrix} C^6H^4Br \\ C^6H^4Br^2 \end{smallmatrix} > CH^3$, is obtained by bringing bromine and fluorene together in such a manner as to avoid rise of temperature, which is effected by slowly passing air charged with bromine-vapour into a solution of fluorene in carbon sulphide. This compound forms silky yellow needles soluble in benzene, but decomposing on frequent crystallisation into hydrobromic acid and dibromofluorene; the same decomposition is instantly produced by alcoholic potash.

Nitrofluorenes. **Mononitrofluorene**, $C^{10}H^7(NO^2)$, is prepared by boiling fluorene for twenty-four hours with ordinary nitric acid diluted with twice its bulk of water. When purified by recrystallisation from a mixture of alcohol and benzene, it forms a red powder which melts, with decomposition, at a somewhat high temperature.

Dinitrofluorene, $C^{10}H^6(NO^2)^2$, is obtained by dissolving fluorene in a mixture of equal volumes of fuming nitric and glacial acetic acid, keeping the solution cool. When separated by water, dried, and crystallised from a mixture of nitrobenzene and light coal-tar oil, it forms reddish-yellow needles, which, if slowly heated, melt with a certain amount of alteration at a temperature above 260° , but decompose with deflagration when rapidly heated.

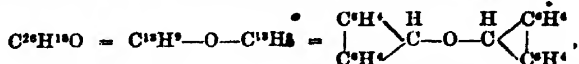
A fluorenesulphonic acid is obtained by heating fluorene with strong sulphuric acid; its salts are either uncrystallisable or crystallise with difficulty.

DIPHENYLENE-METHYLIC or, FLUORENIC ALCOHOL.

$C^{10}H^{10}O = \begin{smallmatrix} C^6H^4 \\ C^6H^4 \end{smallmatrix} > CH(OH)$ (Barbier, *loc. cit.*) This secondary alcohol, which may be

regarded as derived from methyl alcohol, $HCH^3(OH)$, by substitution of the diatomic group, $-C^6H^4-C^6H^4-$, for 2 at. hydrogen, is formed by the action of nascent hydrogen on diphenylene-ketone, $(C^6H^4-C^6H^4)CO$. It is soluble in common alcohol and ether, more easily in benzene, and crystallises from the latter in hexagonal plates melting at 153° . Oxidising agents reconvert it into diphenylene ketone. With acetic anhydride at 100° it forms fluorenic acetate, $C^{10}H^{10}O^2 = \begin{smallmatrix} C^6H^4 \\ C^6H^4 \end{smallmatrix} > CH(OC^2H^3O)$, a crystalline body melting at 75° , and saponifiable by baryta-water at 120° , with formation of barium acetate and reproduction of the alcohol.

Fluorenic alcohol heated to a temperature a little above its melting point, gives up water and is converted into fluorenic oxide or fluorenic ether,



a nearly colourless resinous body, melting at 200° , very soluble in benzene, but only slightly soluble in ordinary alcohol and ether.

DIPHENYLETHANE, $C^{10}H^{12} = H^3C-CH(C^6H^4)^2$ (Goldschmiedt, *Deut. Chem. Ges. Ber.* vi. 1501). This hydrocarbon is obtained by leaving diphenyltrichlorethane in contact with alcohol and sodium-amalgam at a temperature of 30° – 40° . The oily product still contains chlorine, and must therefore be first heated with hydriodic acid and red phosphorus to 210° , and then digested with sodium on a water-bath. Diphenylethane is an oily, limpid, and very refractive liquid, possessing a very agreeable smell, and boiling at 268° – 271° ; in a freezing mixture it solidifies to a crystalline mass. When oxidised with chromic acid solution, it yields diphenyl ketone and a little benzoic acid. When its vapour is passed through a red-hot tube filled with fragments of pumice, stilbene appears to be formed. Bromine acts strongly

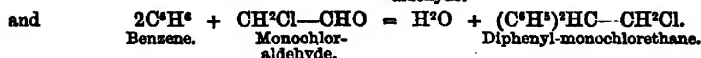
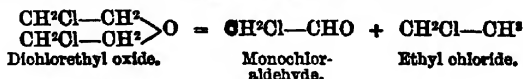
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on diphenylethane. *Fuming nitric acid* dissolves it very readily, and the solution soon deposits crystals, but, on adding water, resinous products are precipitated.

According to Radziszewski (*Deut. Chem. Ges. Ber.* vii. 140), diphenylethane is easily formed by the action of zinc on a mixture of phenylbromomethyl and benzene; it boils at 268° – 270° . At the same time a white fragrant solid body melting at 124° is formed, in greater abundance as the proportion of benzene employed in the reaction is larger.

Diphenyl-monochlorethane, $\text{C}^6\text{H}^5\text{Cl} = (\text{C}^6\text{H}^5)^2\text{HC}-\text{CH}^2\text{Cl}$ (E. Hepp, *Deut. Chem. Ges. Ber.* vi. 1439; vii. 1409). This compound is formed by the action of dichlorethyl-oxide on benzene, in presence of strong sulphuric acid:



On adding sulphuric acid to a mixture of dichlorethyl oxide and benzene, the liquid becomes turbid, and the benzene separates in the form of a light red layer. The addition of sulphuric acid is continued, with constant agitation, and occasional cooling, till the reaction is completed, after which the dark brown mass is left to itself for a day and then poured into water. Diphenylchlorethane then separates as an oil, which may be partially purified by distillation with water, and, if then distilled *per se*, is resolved into HCl and diphenylethylene or stilbene, $\text{C}^6\text{H}^5-\text{CH}=\text{CH}-\text{C}^6\text{H}^5$. By boiling with alcoholic potash, on the other hand, it is converted into isostilbene, $\text{CH}^3-\text{C}(\text{C}^6\text{H}^5)^2$, (p. 678).

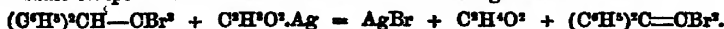
Diphenyl-tribromethane, $(\text{C}^6\text{H}^5)^2\text{HC}-\text{CBr}^3$, is prepared by mixing 1 mol. bromal and 2 mols. benzene with about a double volume of strong sulphuric acid:



The mixture turns first orange-yellow, then brown, finally dingy green, and deposits, especially if the benzene has not been added in excess, a crop of crystals often of considerable size. The mass, having been left for two or three days till it has become pulpy, is poured into water, and the separated crystals, after washing first with cold and then with warm water, are recrystallised from absolute alcohol with addition of animal charcoal.

Diphenyl-tribromethane crystallises from alcohol in needles or laminae, from ether in transparent colourless monoclinic prisms 5 or 6 mm. long. Axial ratio a (clinod.): b (orthod.): $c = 1.21416 : 1 : 0.6043$. Angle $ac = 100^{\circ} 31'$. Observed faces ∞P . $\infty P2$. $\infty P\infty$. $\infty R\infty$. $R\infty$. $4P\infty$. The crystals are developed in the form of thin tablets, sometimes in the direction of the orthopinacoid, sometimes in that of the plane of the optic axes, which is the plane of symmetry. Double refraction positive and weak. The apparent acute angle of the optic axes in air is $111^{\circ} 17'$ for red, 111° for yellow, and $90^{\circ} 51'$ for green light (Hintze, *Pogg. Ann.* clii. 265).

Diphenyl-tribromethane melts at 89° , dissolves easily in ether, chloroform, carbon disulphide, hot glacial acetic acid, and alcohol, less easily in cold alcohol, benzene, and aniline. When heated it decomposes, with separation of hydrogen bromide. Heated with lime it gives off the odour of diphenyl. On boiling diphenyl-bromethane for some time with alcoholic potash in a vessel with reversed condenser, and pouring the mass into water, diphenyl-dibromomethylene, $(\text{C}^6\text{H}^5)^2\text{C}=\text{CBr}^2$, separates in shining needles. The same compound is formed from diphenyl-tribromethane by dry distillation, by heating it to 140° – 150° , with alcoholic ammonia; and by heating it to the same temperature with silver acetate and a little glacial acetic acid:



On heating 5 grams of diphenyl-tribromethane with 20 gr. hydriodic acid, b. p. 127° , and 1.6 gr. red phosphorus for several hours at 170° , an oil was obtained, together with a compound which melted at 80° , and separated from ether in crystals, belonging, according to Hintze's measurement, to the monoclinic system. Axial ratio: a (clinod.): b (orthod.): $c = 1.2221 : 1 : 0.4265$. Angle $ac = 105^{\circ} 21' 40''$. Combination, ∞P . $\infty P\infty$. $R\infty$. This compound, which was obtained in small quantity only, gave by analysis 49.2 per cent. carbon and 3.91 hydrogen, numbers compatible with the formula either of diphenyl-dibromomethylene or of diphenyl-dibromomethylene. When the mixture of diphenyl-tribromomethylene, hydriodic acid, and phosphorus, was heated for seven or eight hours to 210° , a product was formed which appeared from analysis to be a mixture of $\text{C}^6\text{H}^5\text{Br}$ and diphenylethane, C^6H^5 (Goldschmiedt).

~~— Dichlorodiphenyl-ethane, $(C^6H^5)_2HC-CH_2-$~~ , $(C^6H^5)_2HC-CCl_2$, is formed, like the corresponding bromine-compound, by the action of chloral on 1 acid (Baeyer, *Deut. Chem. Ges. Ber.* v. 1097). It has not been obtained in crystalline form, but appears to be isomorphous with diphenyl-tribromomethane (Hintze). It dissolves easily in ether, chloroform, carbon disulphide, hot glacial acetic acid, and alcohol, less easily in cold alcohol, benzene, and aniline. Heated with lime it exhales the odour of diphenyl, and is converted by dry distillation, or by treatment with alcoholic potash, into diphenyl-dichloroethylene, $(C^6H^5)_2C=CCl_2$. In alcoholic solution it is slightly decomposed by boiling with potassium cyanide, with formation of hydrocyanic acid and diphenyl-dichloroethylene. When vapour of diphenyl-trichloroethane is passed over red-hot zinc-dust, stilbene, $C^{10}H_8$, is produced, together with a small quantity of liquid smelling of benzene and diphenyl (Goldschmidt, *Deut. Chem. Ges. Ber.* vi. 985).

Dimonobromophenyl-trichloroethane, $(C^6H^4Br)_2HC-CCl_2$, is prepared by digesting 1 pt. bromobenzene and 2 pts. chloral with 4 or 5 vols. strong sulphuric acid for some time, with frequent agitation and gentle warming of the liquid on the water-bath. As soon as a white tenacious mass ceases to separate from the liquid, a large quantity of water is added, and the oil thereby separated, which solidifies to a crystalline mass on exposure to the air, is washed with water, and recrystallised from hot ether-alcohol.

Dimonobromophenyl-trichloroethane is insoluble in benzene, very sparingly soluble in cold alcohol and glacial acetic acid, more freely in hot alcohol, chloroform, and ether, very easily in carbon disulphide. From alcohol it crystallises in colourless silky needles; from a mixture of alcohol, ether, and chloroform, or from carbon disulphide, in large compact crystals. Melting point, $139^\circ-141^\circ$. By heating with alcoholic potash it is converted into dimonobromophenyl-dichloroethylene, $(C^6H^4Br)_2C=CCl_2$ (O. Zeidler, *Deut. Chem. Ges. Ber.* vii. 1180).

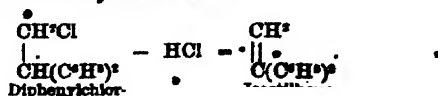
Dinitro-dimonobromophenyl-trichloroethane, $C^{10}H^7Cl_2Br_2(NO_2)_2$ = $[C^6H^3(NO_2)_2Br]_2HC-CCl_2$, obtained by heating the preceding compound with fuming nitric acid till it is completely dissolved, crystallises from alcohol in yellowish prismatic needles melting at $168^\circ-170^\circ$ (Zeidler).

Dimonochlorophenyl-trichloroethane, $(C^6H^4Cl)_2HC-CCl_2$, prepared like the corresponding compound, crystallises from ether-alcohol in white felted needles resembling quinine sulphate, behaves to solvents like the bromine compound, and melts at 105° . By prolonged boiling with alcoholic potash it is converted into dimonochlorophenyl-dichloroethylene, $(C^6H^4Cl)_2C=CCl_2$.

Dinitro-dimono-chlorophenyl-trichloroethylene, $C^{10}H^7Cl(NO_2)_2$ = $[C^6H^3(NO_2)_2Cl]_2HC-CCl_2$, separates from its solutions in fine crystals, from alcohol in needles, and melts at 143° . The crystals (measured by Hintze, *Pogg. Ann.* clii. 265) are monoclinic, with the axial ratio: $a : b = 1.3104 : 1$. Angle $ac = 110^\circ 26'$. Faces, ∞P , $\infty P_50, 0P$. The dark yellow crystals are moderately transparent, shortly prismatic, scarcely 1 mm. long. The plane of symmetry is the plane of the optic axes. The axis of greatest elasticity makes in that plane an angle of about $28^\circ 22'$ with the transverse face, and is the first median line. Double refraction negative and strong. Dispersion $p < v$. The apparent acute angle of the optic axes in air is about 58° .

Dinitro-dimono-chlorophenyl-trichloroethane yields, with alcoholic ammonium sulphide, a product crystallising from acetone in small yellow needles (Zeidler).

DIPHENYL-ETHYLENE, $C^{10}H_8 = C^6H_5(C^6H_5)_2$.—Of this hydrocarbon there are two modifications, viz. stilbene, boiling at $306^\circ-307^\circ$, and isostilbene at 277° . Both are formed by abstraction of HCl from diphenyl-monochloroethane, $CH_2Cl-CH(C^6H_5)_2$, the former by the action of heat alone, the latter by boiling with alcoholic potash. Now, as this last reaction takes place with great facility and at a moderate heat, the resulting diphenylethene has doubtless a constitution similar to that of the diphenylchloroethane, that is to say, with both its phenyl-atoms attached to the same carbon-atom of the ethylene-molecule:

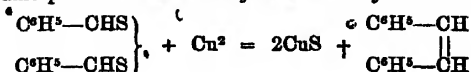


and hence it must be inferred that in the formation of stilbene from the same compound, which takes place at a much higher temperature, a molecular transformation occurs, resulting in the formation of the symmetrical molecule, $C^6H_5-CH=CH-C^6H_5$,
x x 2

in which each of the phenyl-atoms is attached to a separate carbon-atom of the ethylene (Hepp, *Deut. Chem. Ges. Ber.* vii. 1409).

Stilbene is also formed by the following reactions:

a. By heating amorphous thiobenzaldehyde with finely divided copper:



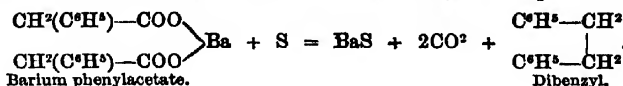
(Klinger, *Deut. Chem. Ges. Ber.* ix. 1892).

β. By passing the vapour of diphenylethane, $\text{C}^{14}\text{H}^{14}$, through a red-hot tube filled with fragments of pumice, or that of diphenyl-trichlorethane, $\text{C}^{14}\text{H}^{11}\text{Cl}_3$, over red-hot zinc-dust (Goldschmiedt, *Deut. Chem. Ges. Ber.* vi. 915, 1501).

γ. Together with toluene, by heating dibenzyl in sealed tubes: $2\text{C}^{14}\text{H}^{14} = \text{C}^{14}\text{H}^{12} + 2\text{C}^7\text{H}_8$ (Barbier, *Ann. Ch. Phys.* [5], vii. 472).

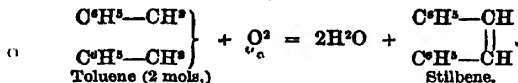
δ. By heating toluene, C^7H_8 , to $170^\circ\text{--}180^\circ$ with hydriodic acid and red phosphorus, diphenyl being also produced if the action be prolonged (Barbier, *Compt. rend.* lxxviii. 1772).

ε. By heating 1 pt. dibenzyl with $\frac{1}{2}$ pt. sulphur: $\text{C}^{14}\text{H}^{14} + \text{S} = \text{SH}_2 + \text{C}^{14}\text{H}^{12}$ (Radziszewski, *Deut. Chem. Ges. Ber.* viii. 758). Hence also it is obtained by distilling barium phenylacetate (α-toluate) with a slight excess of sulphur, instead of dibenzyl which is formed, in the first instance, according to the equation:



The solidified distillate, when pressed and crystallised from alcohol and ether, yields a large quantity of pure stilbene. Phenylacetate of lead, distilled with a large excess of sulphur, likewise yields stilbene, together with an easily fusible substance (Radziszewski, *ibid.* vi. 390).

ζ. By passing the vapour of toluene over heated lead oxide (Behr a. van Dorp, *ibid.* 1501):

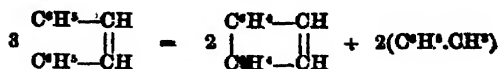


This reaction affords a confirmation of the constitutional formula above assigned to stilbene.

To prepare stilbene by this method, vapour of toluene is slowly passed (1 drop volatilised in ten seconds) over lead oxide heated to dull redness in an iron tube. The solid-portion of the distillate consists mainly of stilbene, the liquid portion of a solution of stilbene and other hydrocarbons in toluene. The product remaining after distilling off the toluene is mixed with the solid mass first obtained, and the whole is once crystallised from alcohol, whereby perfectly pure stilbene is obtained amounting to 16 per cent. of the toluene employed. As bye-products of the reaction are formed, diphenyl (probably from benzene mixed with the toluene), phenanthrene, anthracene, and liquid hydrocarbons probably consisting mainly of ditolyl.

C. Forst (*Liebig's Annalen*, clxxviii. 370; *Fahresb. f. Chem.* 1875, 401) has compared the different methods recommended for the preparation of stilbene, and gives the preference to that of Märcker, which consists in the decomposition of benzyl sulphide, $\text{C}^{14}\text{H}^{14}\text{S}$, and disulphide, $\text{C}^{14}\text{H}_8\text{S}_2$, by heat (v. 859). Benzyl chloride is first produced by passing dry chlorine into nearly boiling toluene; the portion of the product which boils between 175° and 210° is added to an alcoholic solution of potassium sulphide; and the sulphur-compounds, which separate on distilling off the alcohol, are heated in small retorts over a charcoal fire, as long as anything passes over without the application of too high a temperature. The solidified distillate is freed by pressure from oily substances, and, when once redistilled and crystallised from alcohol, yields pure stilbene amounting to 9 or 10 per cent. of the benzyl chloride used. Radziszewski's method of distilling barium phenylacetate with sulphur, easily yields, according to Forst, a pure product, but the amount is not satisfactory. Lorenz's method (passing toluene vapour over heated lead oxide) yields, according to Forst, only a small quantity of stilbene, but large quantities of tarry and resinous products. Lorenz, however, maintains that when the process is properly conducted these products are not formed. From 100 grams of toluene Lorenz obtained 18 grms. stilbene.

Stilbene melts at 120° (Brunner, *Liebig's Annalen*, cli. 133) and boils at $306^\circ\text{--}307^\circ$. Its vapour passed through a red-hot tube is resolved into phenanthrene and toluene:



(Graebe, *Deut. Chem. Ges. Ber.* vi. 494).

On the Decomposition of Stilbene Bromide by Potassium Acetate and Alcohol, *see* HYDROBENZOÏN (p. 680).

Nitro-derivatives of Stilbens. *Dinitrostilbene*, $C^{14}H^{10}(NO_2)^2$, $C^6H^4(NO_2)-CH=CH-C^6H^4(NO_2)$, may be prepared by dissolving nitrobenz chloride, $C^6H^4(NO_2)Cl$, in warm alcohol, mixing the solution with excess of aqueous potash, filtering off the sulphur-yellow flocks which separate, and crystallising the from alcohol. The dinitro-compound crystallises in shining yellow needles having green shimmer, very slightly soluble in alcohol, almost insoluble in ether and in benzene, somewhat freely soluble in nitrobenzene. Hot glacial acetic acid likewise dissolves it in considerable quantity, and deposits it, for the most part, on cooling, in warty groups of crystals. It melts at 280° to a liquid which on cooling solidifies to a crystalline mass. It sublimes in yellow laminae. With nitric acid it yields yellow resinous products, and when boiled with alcoholic potash it is converted into a brown amorphous mass insoluble in all the ordinary solvents. By boiling with alcoholic ammonium sulphide it is converted into amidostilbene, $C^{14}H^{12}(NH)^2$, and, when heated therewith to 100° , into diamidostilbene, $C^{14}H^{14}(NH_2)^2$ (J. Strakosch, *Deut. Chem. Ges. Ber.* vi. 328).

When 1 pt. of stibene is dissolved in 26 pts. of ether, and 7 pts. of fuming nitric acid are added by drops to the well-cooled solution, a compound, $\text{O}^i\text{H}^{11}\text{N}^0\text{O}^4$, is formed which separates after twenty-four hours in concentric groups of white needles. It is soluble in glacial acetic acid, and crystallises therefrom also in needles; insoluble in benzene, chloroform, ether, and carbon disulphide. It melts at 220° , giving off red fumes, and is decomposed in a similar manner by strong sulphuric acid. Bromine, nascent hydrogen and oxidising mixtures act upon it but slowly. By boiling with alcohol it is converted into another compound, which gives by analysis numbers leading to the empirical formula, $\text{C}_2\text{H}^{12}\text{N}^0\text{O}^4$; crystallises from the alcoholic solution by spontaneous evaporation in silky white needles; melts without decomposition between 60° and 70° , after gradual softening; and dissolves readily in alcohol and ether. The mother-liquor of the white substance which separates from the ethereal solution of stibene on treatment with nitric acid, yields, on spontaneous evaporation of the ether, recrystallisation of the residue from glacial acetic acid, and evaporation of that solvent, an oil having a strong odour of bitter almonds, and a compound which crystallises in large colourless prisms melting at 123° – 125° (Lorenz, *Dout. Chem. Ges. Ber.* vii, 1096).

The compound $C^6H^{11}N^2O^2$, heated to 150° with hydrochloric acid, yields benzoic acid, nitrobenzene, a gas which turns red in contact with oxygen, and a non-acetified body crystallizing in needles. Water acts on this nitro-compound in the same way as hydrochloric acid. By prolonged boiling with alcohol or by heating therewith to 100° – 120° in sealed tubes it is converted into a wine-yellow compound. Other alcohols act upon it in a similar manner (Lorenz & Blumenthal, *ibid.* viii. 1050).

Amidostilbenes (Strakosch, *Deut. Chem. Ges. Ber.* vi. 329).
(NH₂) and *Diamidostilbene*,
reducing dinitrostilbene with ammo-
stilbene is heated for a short time in
an open vessel with alcoholic ammonium sulphide till the liquid assumes a dark red
colour; the alcohol is then distilled off; the residue exhausted with strong hydrochloric
acid; the liquid filtered from sulphur and unaltered dinitrostilbene is mixed with
caustic soda; and the resulting precipitate is freed from diamidostilbene by washing
with dilute hydrochloric acid, and recrystallisation from nitrobenzene.

Nitroamidostilbene crystallises from hot nitrobenzene in purple-red leaflets. It is very slightly soluble in alcohol, ether, or benzene, insoluble in water. When heated to 229°-230°, it melts, and at a higher temperature sublimes in red leaflets. Hot hydrochloric acid dissolves it, and, on cooling, a hydrochloride, $C^{14}H^{11}N^2O^4.HCl$, is deposited in shining yellow needles. This salt is decomposed by water, or by heating, with separation of hydrochloric acid, but crystallises unaltered from alcohol containing hydrochloric acid. An attempt to prepare the platinumchloride was unsuccessful.

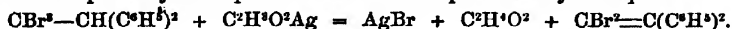
Diamdostilbene, $C_8H_{10}(NH_2)_2$, is obtained by heating dinitrostilbene with alcoholic ammonium sulphide to 100° for about half an hour in a sealed tube, then distilling off the alcohol, exhausting the residue with hydrochloric acid, and precipitating with an alkali. On crystallising the precipitate from dilute alcohol, the base is obtained in shining leaflets, which soon turn brown on exposure to the air. It dissolves with

difficulty in benzene, ether, and water. At 170° it melts and becomes brown, and at a higher temperature sublimes in white leaflets, with partial decomposition. The *hydrochloride*, $C^{14}H^{10}(NH^2)^2 \cdot 2HCl$, crystallises in large white leaflets easily soluble in water and hot hydrochloric acid, and slightly soluble in alcohol. The *sulphate* forms needles easily soluble in water and in dilute sulphuric acid. The *nitrate* forms yellow granular crystals which dissolve readily in water, and in alcohol. The dark red amorphous *platinocloride* is insoluble in water, but soluble in hot alcohol.

Isostilbene, $CH^2=C(C^6H^5)^2$ (Hepp, *Deut. Chem. Ges. Ber.* vii. 1409). This modification of diphenylethylene is formed, as already observed, by boiling diphenyl-monochlorethane, $CH^2Cl-CH(C^6H^5)^2$, with alcoholic potash. It is a colourless, strongly refracting oil, having a high specific gravity and pleasant odour; becomes somewhat viscid at the temperature of a mixture of ice and salt; boils at 277° ; is insoluble in water, but mixes in all proportions with alcohol and ether. When boiled with chromic acid mixture, it yields benzophenone together with carbon dioxide and water. When its vapour is passed through a red-hot tube, much charcoal is separated and a distillate is obtained, which smells of benzene and diphenyl, and solidifies, as the benzene evaporates to a pitchy mass, which does not appear to contain stilbene; neither is stilbene produced by passing the vapour of isostilbene mixed with hydrochloric acid through a red-hot tube.

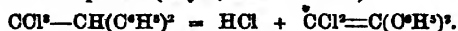
Bromisostilbene or **Diphenyl-monobromethylene**, $CHBr=C(C^6H^5)^2$, is formed by adding isostilbene to a solution of bromine in carbon disulphide as long as the liquid is decolorised thereby, that is, till 1 mol. stilbene has been added for each molecule of bromine (Br^2). A brisk evolution of hydrogen bromide then takes place after a while, and on evaporating the solvent there remains a colourless oil, probably $CH^2Br-CBr(C^6H^5)^2$, which is resolved, on exposure to the air, or more quickly when heated, into hydrogen bromide and bromisostilbene. This compound forms prisms about an inch long; melts at 50° ; distils above 300° ; dissolves sparingly in cold alcohol, easily in ether, acetone, and carbon sulphide; crystallises therefrom with difficulty, and easily exhibits the phenomenon of superfusion. It does not unite with bromine, and is but slowly attacked by chromic acid mixture (Hepp, *loc. cit.*)

Dibromisostilbene or **Diphenyl-dibromethylene**, $CBR^2=C(C^6H^5)^2$, is formed by boiling diphenyl-tribromethane, $CBR^3-CH(C^6H^5)^2$ for some time with alcoholic potash in a vessel with reversed condenser; separates on pouring the mass into water, in small shining needles; and may be obtained by recrystallisation from ether-alcohol in needles an inch long. It is also produced from diphenyl-tribromethane by dry distillation, by heating to 140° – 150° with alcoholic ammonia, and by the action of silver acetate and a little glacial acetic acid at the same temperature. This last reaction probably takes place in the manner represented by the equation



Diphenyl-dibromethane melts at 83° , and boils with slight decomposition above 300° . It dissolves easily in ether, chloroform, and carbon sulphide, less easily in benzene and in alcohol. It does not unite with bromine, even when heated to 140° in a solution thereof in carbon sulphide (Goldschmidt, *Deut. Chem. Ges. Ber.* vi. 985).

Dichlorisostilbene or **Diphenyl-dichlorethylene**, $CCl^2=C(C^6H^5)^2$, is obtained by subjecting diphenyl-trichlorethane to dry distillation (Goldschmidt), or by boiling it with alcoholic potash (Bayer, *ibid.* vi. 922a):



Dichlorisostilbene distils almost without decomposition, dissolves easily in ether, chloroform, and carbon sulphide, less easily in alcohol, and in benzene. From hot alcohol it separates in flat prisms an inch long, from a cold and not too concentrated alcoholic solution in very well defined prisms; from ether-alcohol in long needles. These three kinds of crystals exhibit identical forms and belong, according to Hintze's measurements (*Pogg. Ann.* clii. 265) to the monoclinic system. Axial ratio, $a : b : c = 1.3367 : 1 : 1.7588$. Angle $\alpha c = 119^{\circ} 46'$. Observed combination, $0P. \infty P. \infty. + \frac{1}{2}P. \infty. + P. + \frac{1}{2}P. + 2R^4$. The crystals are elongated in the direction of the axis of symmetry, cleave parallel to the base, and form twins in the same direction. Double refraction strong and negative. The plane of the optic axes is perpendicular to the plane of symmetry, nearly normal to the base, and the first medium line is perpendicular to the axis of symmetry. The interior of the crystals is always filled with twin-lamellae, so that the interference phenomena of the optic axes are very much disturbed, and only approximate measurements of these angles could be obtained, viz. in air for red light, $29^{\circ} 38'$; for yellow, $30^{\circ} 50'$; for green, $31^{\circ} 12'$. The crystals melt at 79° (Hintze).

Dimonobromophenyl-dichlorethylene, $CCl^2=C(C^6H^4Br)^2$, is produced by

heating dimonobromophenyl-trichlorethane (p. 676) with alcoholic potash for ten hours, and may be obtained by washing with water and repeated crystallisation from alcohol in colourless needles. It dissolves easily in hot alcohol, ether, and chloroform, and in carbon sulphide, separates from the latter in large shining crystals, and melts at 119° – 120° (Goldschmiedt). The crystals are orthorhombic, with the axial ratio $a : b : c = 0.42106 : 1 : 0.62080$. Observed faces, ∞P , ∞P_2 , ∞P_3 , ∞P_4 , ∞P_5 , ∞P_6 , ∞P_7 , ∞P_8 . The crystals are of the same habit, and exhibit the same striation as those of the analogous chlorine-derivative (*infra*), but they are all much smaller. The plane of the optic axes is the base; the first median line, the brachydiagonal. Double refraction moderately strong and positive, dispersion of the axes very considerable. The acute apparent angle of the axes is in air, for red light, $37^{\circ} 28'$; for yellow, $34^{\circ} 22'$; for green, $29^{\circ} 31'$. Melting point, 119° – 120° (Hintze).

Dimonochlorophenyl-dichlorethylene, $\text{CCl}_2=\text{C}(\text{C}^*\text{H}^*\text{Cl})_2$, prepared by boiling dimonochlorophenyl-trichlorethane with alcoholic potash, resembles the bromine-compound, and separates from its alcoholic solution on evaporation in crystals having a diamond lustre and melting at 89° (Goldschmiedt). The crystals belong to the orthorhombic system, with the axial ratio $0.42456 : 1 : 0.61222$. Observed faces ∞P , ∞P_2 , ∞P_3 , ∞P_4 , ∞P_5 , ∞P_6 , ∞P_7 , ∞P_8 , ∞P_9 , ∞P_{10} , ∞P_{11} , ∞P_{12} . The plane of the optic axes is the brachypinacoid; the first median line the brachydiagonal. The double refraction is moderately strong and positive, the dispersion of the axes very considerable. The acute apparent axial angle in air is, for red light, $33^{\circ} 32'$; for yellow, $34^{\circ} 28'$; for green, $38^{\circ} 57'$ (Hintze).

Dimonochloro-diphenyl-ethylene, $\text{OH}^2=\text{C}(\text{C}^*\text{H}^*\text{Cl})_2$, appears to be formed by dry distillation of the compound $\text{OH}^2\text{Cl}-\text{OH}(\text{C}^*\text{H}^*\text{Cl})_2$, resulting from the action of strong sulphuric acid on a mixture of monochloraldehyde and monochlorobenzene. It is an oil boiling between 280° and 285° , very easily attacked by sodium, uniting with bromine less easily than diphenylethylene, and rather slowly oxidised by chromic acid mixture without production of an aromatic acid (Hepp, *Deut. Chem. Ges. Ber.* vii. 1419).

A comparison of the crystalline forms of the compounds above described (pp. 674–679) shows that the compounds formed by the union of aldehydic bodies (acetaldehyde, chloral, bromal acid), and aromatic hydrocarbons, with elimination of hydrogen, crystallise in monoclinic forms when the aromatic hydrocarbon retains its original hydrogen-atoms unreplaced, the aldehyde at the same time having any number of its hydrogen-atoms replaced by chlorine or bromine; but that the union of aldehydic bodies with aromatic hydrocarbons in which the hydrogen is more or less replaced by Cl, Br, &c. gives rise to compounds which crystallise in the orthorhombic system. In the analogous chlorine and bromine-compounds thus formed, the chlorine and bromine occupy corresponding places in the molecule, and the resulting compounds are isomorphous (Hintze).

Diphenylene or Stilbene Alcohols, Hydrobenzoins. $\text{C}^*\text{H}^*\text{H}^*\text{O} = \text{C}^*\text{H}^*\text{H}^*(\text{OH})$ (Forst a. Zincke, *Deut. Chem. Ges. Ber.* vii. 1708; *Likbig's Annalen*, clxxxii. 241). No fewer than six bodies having this composition have been described by different chemists, viz. (1). Zinin's hydrobenzoin, obtained by the action of zinc and alcoholic hydrochloric acid on benzaldehyde; formed also, according to Fittig a. Ammann, by the action of sodium-amalgam on the same substance in presence of water or alcohol. (2). Iso-

(4 and 5). Limpricht a. Schwannert's toluylene and isotoluylene alcohols, obtained by treating stilbene bromide with silver acetate and glacial acetic acid, and saponifying the product. (6). Stilbene alcohol, produced by the action of alcoholic potash on benzoin (compare 1st Suppl. 333; 2nd Suppl. 171).

Forst a. Zincke, however, on repeating the processes by which these various bodies are said to have been formed, have come to the conclusion that bitter almond oil, benzoin, and stilbene yield by known methods only two alcohols, namely, the hydrobenzoin of Zinin and the isohydrobenzoin of Fittig a. Ammann. Bitter almond oil yields both these products simultaneously; benzoin yields only hydrobenzoin, whilst stilbene bromide yields one or the other according to circumstances. The so-called dicresol and the toluylene alcohols appear to be mixtures of hydrobenzoin and isohydrobenzoin.

HYDROBENZOINS (Stilbene Alcohols) from Benzoic Aldehyde.—Forst a. Zincke obtained these compounds: (1). By the action of sodium-amalgam on bitter almond oil in presence of water (the best proportion being 1 of the aldehyde to 4 of water). (2). By the action of sodium-amalgam on an ethereal solution of benzoic aldehyde. (3). By the action of sodium amalgam on benzoic aldehyde in presence of acetic acid.

In all cases the product is a mixture of hydrobenzoin and isohydrobenzoin, no other well-defined substance being formed.

Hydrobenzoin from Benzoin and Benzil.—Benzoin treated with sodium-amalgam in presence of alcohol or water yields hydrobenzoin but no isohydrobenzoin, some benzoic acid being formed at the same time.

Benzil, when heated with sodium-amalgam and water, yields a large quantity of hydrobenzoin, together with a small quantity of a body crystallising in needles which melt at 60°.

Hydrobenzoin from Stilbene Bromide.—Stilbene bromide, when heated with silver acetate and glacial acetic acid, yields the diacetates of hydrobenzoin and isohydrobenzoin, and monoacetate of isohydrobenzoin. These three products are separable by fractional precipitation with water; by saponification with alcoholic potash they yield hydrobenzoin and isohydrobenzoin, the former preponderating.

Stilbene bromide, heated to 160° with potassium acetate and glacial acetic acid, yields isohydrobenzoin diacetate and monoacetate, but no hydrobenzoin acetate. When alcohol is substituted for glacial acetic acid, the product is a mixture of stilbene and monobromostilbene.

Stilbene bromide, heated with silver benzoate in xylene, yields hydrobenzoin and isohydrobenzoin dibenzoates, the former preponderating.

Stilbene bromide, treated with silver oxalate in xylene, yields a large quantity of stilbene, and a number of resinous products, which by saponification with alcoholic ammonia give almost exclusively hydrobenzoin.

The distinguishing characteristics of these two alcohols and their derivatives are exhibited in the following table:

Hydrobenzoin.

Isohydrobenzoin.

Alcohols, $C^{14}H^{12}(OH)^2$.

Melts at 134°, and crystallises from hot acetic acid or dilute alcohol in fine glittering laminae, and from hot absolute alcohol in large, thin, transparent, rhombohedral tablets, which latter are obtained also by slow evaporation of its solution in benzene, benzolin, or chloroform.

Dissolves easily in alcohol, ether, and chloroform, and is deposited therefrom in well-formed crystals. From hot water it separates sometimes in hydrated, sometimes in anhydrous crystals. The hydrated crystals are clear and colourless, and melt at 95°–96°. The anhydrous crystals, which are monoclinic, melt at 119°–120°.

Dibromides, $C^{14}H^{12}Br^2$.

Sparingly soluble in alcohol and ether; m. p. 233°.

Sparingly soluble in alcohol and ether; m. p. 232°.

Monoacetates, $C^{14}H^{11}.OH.C^2H^3O^2$

From hydrobenzoin by the action of acetic acid. Long needles, easily soluble in alcohol; melting at 84°.

From stilbene bromide with acetate of potassium or of silver. Short, thick needles easily soluble in alcohol; melting at 87°–88°.

Diacetates, $C^{14}H^{12}(C^2H^3O^2)^2$.

From stilbene bromide with silver acetate; from benzaldehyde hydrobenzoin, by the action of acetyl chloride and acetic acid. Fine prismatic crystals moderately soluble in hot, less in cold alcohol; m. p. 134°.

From stilbene bromide with silver acetate, and with potassium acetate; from the monoacetate by acetic anhydride; from isohydrobenzoin with acetic anhydride. Crystallises in laminae or well-defined prisms, both apparently rhombic. The laminae melt constantly at 117°–118°; the prisms, also, at 117°–116° the first time; but the second or third at 105°–106°. Prismatic crystals, obtained by recrystallisation of the laminae, exhibit the same behaviour, melting the second time at 105°–106°.

DIPHENYL-ETHYLENE CHLORIDES.

Hydrobenzoin.

Monobenzoates, $C^6H^5(OH)(OC^6H^5O)$.

Formed, together with the dibenzoate, by heating hydrobenzoin to 150° – 160° , with benzoic anhydride. Slender brilliant needles or laminae, which melt at 160° – 161° , and dissolve easily in hot alcohol, ether, or chloroform.

Is hydrobenzoin.

Obtained, in very small quantity only, by the same reaction as the hydrobenzoin compound. Crystallises from weak spirit in small shining needles, which melt at 130° and dissolve in ether and in chloroform.

Dibenzoates, $C^6H^5(C^6H^5O)^2$.

From stilbene bromide with silver benzoate: from hydrobenzoin with benzoyl chloride. Small needles, very slightly soluble in hot alcohol, more easily in hot acetic acid; m. p. 246° – 247° .

From stilbene bromide with silver benzoate, not with benzoyl chloride. White, brittle needles, easily soluble in hot alcohol; m. p. 153° – 154° .

Is hydrobenzoin monobenzoate is also formed in small quantity when is hydrobenzoin is heated to 150° – 160° with excess of benzoic anhydride, the dibenzoate and hydrobenzoin being produced at the same time; so that in this reaction there is a direct transformation of is hydrobenzoin into hydrobenzoin.

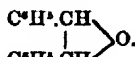
Action of Dilute Sulphuric acid on the Stilbene Alcohols (Zincke & Breuer, *Deut. Chem. Ges. Ber.* ix. 1769). Each of these alcohols when thus treated yields a liquid and a solid product. The liquid obtained from both is the same, viz., diphenyl-acetaldehyde, $(C^6H^5)_2CH-OH-CHO$ (p. 665). The solid products are not identical; that obtained from hydrobenzoin crystallises from hot alcohol in glistening needles melting at 131° – 132° , whereas the product from is hydrobenzoin crystallises from alcohol in spherical groups of small needles melting at 100° – 101° . Both these products are but slowly oxidised by chromic acid mixture, a small quantity of benzoic acid being formed. A solution of chromic trioxide in acetic acid acts more energetically, but forms only very small quantities of benzaldehyde and benzoic acid, the chief products consisting of crystalline neutral bodies, which appear to be identical.

From these results it appears that hydrobenzoin and is hydrobenzoin have the same chemical constitution, being in fact physical isomerides, as are also the solid products formed from them by the action of dilute sulphuric acid.

The two stilbene alcohols may be regarded as diphenyl-glycol, and their transformation into diphenyl-acetaldehyde is precisely analogous to that of ethylene glycol into acetaldehyde, and to that of pinacone (tetramethylglycol) into pinacolin.



Stilbene
alcohols.



Diphenyl-
acetaldehyde.

DIPHENYL-ETHYLENE CHLORIDES or STILBENE CHLORIDES

$C^6H^5Cl^2$ (Zincke, *Ber.* x. 999). These compounds are formed by the action of phosphorus pentachloride on the stilbene alcohols. Hydrobenzoin thus treated yields two chlorides, one melting at 191° – 192° and the second at 93° – 94° . Is hydrobenzoin yields only the high-melting chloride and a considerable quantity of a resinous body containing chlorine. The first chloride is sparingly soluble in hot alcohol, from which it crystallises in slender needles; a solution in toluene yields larger prismatic crystals, and by the slow evaporation of a solution in ether or chloroform well-defined crystals are obtained. On heating this chloride repeatedly above 200° , the melting point is lowered to 160° – 165° . The chloride melting at 93° – 94° is more readily soluble than the first, and crystallises from alcohol or petroleum-naphtha in four- or six-sided plates or prisms, having an aromatic odour. On heating it several times above its melting point, the latter rises and becomes constant at 160° – 165° . The chloride now consists, as does also that obtained by heating the higher-melting modification, of a mixture of the latter with a more soluble lower-melting chloride, which is probably identical with that having the melting point 93° – 94° .

Phosphorus trichloride converts both alcohols into the chloride melting at 191° – 192° . The acetate formed by the action of silver acetate on this, as well as on the other modification, yields by saponification, is hydrobenzoin, and only a trace of its isomeride.

DIPHENYL-GLYCOLLIC ACID, $C^{12}H^{10}O^2 = (C^6H^5)_2COH-COOH$. On the formation of this acid from diphenylacetic acid, and its identity with benzilic acid, see p. 665.

DIPHENYL-GUANIDINE. See GUANIDINE.

DIPHENYL-LINE, $C^{12}H^8(NH^2)^2$. *Isodiamidodiphenyl*.—This base is formed by reduction of isoamidonitrodiphenyl (p. 662), with tin and hydrochloric acid. The crude product, after precipitation of the tin with hydrogen sulphide, is treated with ammonia to throw down the diphenylamine, and the resulting white precipitate is crystallised from alcohol.

Diphenylamine crystallises in large shining laminae, melting at 53° , sparingly soluble in cold, more easily in boiling water, easily also in alcohol and ether. Its salts are all sparingly soluble in cold water, and crystallise in needles or in plates. With oxidising agents (chromic acid, permanganate, chlorine-water) they yield brown-black precipitates (G. Schultz, *Deut. Chem. Ges. Ber.* ix. 347).

DIPHENYL-KETONE, $C^{12}H^{10}O = C^6H^5-CO-C^6H^5$. *Benzophenone*.—This compound, heated with zinc-dust, yields three hydrocarbons, viz.:

Diphenyl-methane	$C^{12}H^{12} = CH^2(C^6H^5)^2$
Tetraphenyl-ethane	$C^{20}H^{22} = C^2H^2(C^6H^5)^4$
Tetraphenyl-ethylene	$C^{20}H^{18} = C^2(C^6H^5)^4$

(Staedel, *Deut. Chem. Ges. Ber.* vi. 1401; ix. 562).

Diphenyl-ketone heated with *alcoholic potash* is converted into diphenyl-carbinol, $C^6H^5-CHOH-C^6H^5$ (Zagoumeny, p. 666).^o Heated with *fuming sulphuric acid*, it yields, in addition to benzophenonesulphonic acid (*2nd Suppl.* 176), a body having the composition $C^{12}H^8SO^4$, and probably related to diphenyl-ketone in the same manner as sulphobenzide to benzene. This compound is soluble in alcohol, and very soluble in ether and in chloroform, from which it crystallises in needles or prisms melting at $186^\circ-187^\circ$.

On pulverising these crystals, and heating the powder with water in a sealed tube for several days to $180^\circ-200^\circ$, the water on cooling was found to be traversed by long, thin, slightly yellow needles, which, on recrystallisation from a mixture of ether and alcohol, yielded short, thick, four-sided, lemon-yellow prisms, melting at $174^\circ-175^\circ$, and having the composition of the original substance. The watery liquid from which these crystals had separated was neutral, and left on evaporation only a very small quantity of a substance containing sulphur (Beckmann, *Deut. Chem. Ges. Ber.* vi. 1112; viii. 992).

Disulphodichlorophenyl-ketone, or *Sulphochlorobenzophenone*, $C^{12}H^8Cl^2SO^2 = CO(C^6H^4SO^2Cl)^2$, also called *Benzophenone-disulphochloride*, is produced by the action of phosphorus pentachloride on the sodium salt of benzophenonedisulphonic acid (*2nd Suppl.* 176). The product, freed from adhering phosphorus-compounds by washing with water, is at first a honey-yellow liquid, but afterwards becomes viscid and finally solidifies. When dried and treated with carbon sulphide it crumbles to a white powder, and on recrystallising this substance from ether, the disulphodichlorophenyl ketone is obtained in white microscopic prisms melting at 121.5° . By reduction with tin and hydrochloric acid it is converted into a hydro-sulphide (Beckmann).

DIPHENYL-METHANE or **BENZYL-BENZENE**, $C^{12}H^{12} = C^6H^5.CH^2.C^6H^5$. This hydrocarbon is formed: 1. Together with others of higher boiling point, by the action of sulphuric acid on a mixture of benzene and benzyl alcohol:



(Meyer a. Wurster, *Deut. Chem. Ges. Ber.* vi. 963). 2. Together with dibenzyl-benzene, by heating benzyl chloride with benzene and zinc-dust (Zincke, *ibid.* iv. 298):



3. Together with tetraphenyl-ethylene, $C^{20}H^{18}$, and tetraphenyl-ethane, $C^{20}H^{22}$, by heating diphenyl-ketone with zinc-dust: $CO(C^6H^5)^2 + 2H^2 = H^2O + CH^2(C^6H^5)^2$ (Staedel, *ibid.* v. 1401). According to Barbier (*Compt. rend.* lxxix. 812) this process yields a liquid hydrocarbon boiling at $269^\circ-270^\circ$, and differing in its properties and modes of decomposition from diphenyl-methane. Staedel, however, finds by further experiments (*Ber.* vii. 1480), that the chief product of the reaction (90 per cent. of the whole) consists of diphenyl-methane, agreeing in melting point (26°), boiling point (263°), and all its other properties with that obtained by Zincke's process. The hydrocarbon prepared in either way forms a diphenyl-methane-disulphonic acid, $C^{12}H^{10}(SO^2H)^2$, whose potassium salt fused with potassium hydroxide yields a body which crystallises

splendidly from alcohol and ether and appears to consist of dihydroxyphenyl-methane, $\text{CH}_2(\text{C}^6\text{H}_4\text{OH})_2$. 4. By heating diphenyl-ketone to $130^\circ\text{--}140^\circ$ for six hours with hydriodic acid (b. p. 127°) and amorphous phosphorus (Graebe, *Ber.* vii. 1628):



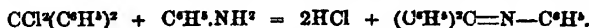
Diphenyl-methane passed through a red-hot tube, gives up 2 at. hydrogen, and is converted into diphenylene-methane, $\text{CH}_2(\text{C}^6\text{H}_4)_2$ (Graebe, *ibid.* 1628). By the prolonged action of chlorine, in presence of iodine, it is converted into perchloromethane and perchlorobenzene (Ruff, *ibid.* ix. 1048).

On the reaction of diphenyl-methane with formaldehyde, see 2nd Suppl. 583.

Diphenyl-chloromethane, $(\text{C}^6\text{H}_5)_2\text{CHCl}$, is formed when hydrochloric acid gas is passed into diphenyl-carbinol, $(\text{C}^6\text{H}_5)_2\text{CHOH}$, fused at as low a temperature as possible. The product solidifies partially on cooling to a radio-crystalline mass, which melts at 14° , and is easily resolved at a higher temperature into hydrochloric acid and tetraphenyl-ethylene, $2(\text{C}^6\text{H}_5)_2\text{CHCl} = 2\text{HCl} + \text{C}^6\text{H}_5)_2\text{C}=\text{C}^6\text{H}_5$ (Engler a. Bettge, *ibid.* vii. 1480).

Diphenyl-dichloromethane or Benzophenonic Chloride, $\text{CCl}_2(\text{C}^6\text{H}_5)_2$, is produced by heating diphenyl-ketone with phosphorus pentachloride. Behr, who first obtained it (2nd Suppl. 176), was unable to purify it, as he found that it was decomposed both by heat and by the action of water. But Kekulé a. Franchimont (*Deutsch. Chem. Ges. Ber.* v. 908) find that by heating benzophenone with phosphorus pentachloride for an hour or two in a flask with reversed condenser, and distilling the product under diminished pressure in a slow current of air, the diphenyl-dichloromethane is obtained quite pure. It is then a colourless, strongly refractive liquid, which boils constantly at 220° under a pressure of 671 mm., and at 305° , with slight decomposition, under ordinary pressure. Water decomposes it slowly in the cold, quickly when heated, forming benzophenone and hydrochloric acid.

Reactions with Aromatic Bases (Pauly, *Liebig's Annalen*, cxxxvii. 198). When 1 mol. diphenyl-dichloromethane is made to act upon 4 mols. of aniline, the mixture being carefully cooled, a brisk reaction takes place, and the whole is converted into a crystalline mass consisting of the diphenyl-methene-aniline, formed according to the equation,



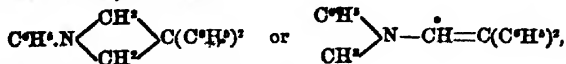
By treating the product with water and ether, then evaporating off the ether, and crystallising the residue from hot absolute alcohol, the diphenyl-methene-aniline is obtained in rhombic crystals melting at 109° , and volatilising without decomposition at a temperature above the boiling point of mercury. It is the phenylic derivative of the compound $\text{C}^6\text{H}_5-\text{N}=\text{CHC}^6\text{H}_5$, called *benzoylaniline* by Laurent a. Gerhardt, who discovered it (*Compt. rend. des travaux de chimie*, 1850, p. 117), and *ditoluidine-diphenylamine* by Schiff, who doubles the formula (*Liebig's Annalen*, Suppl. iii. 343).

Diphenyl-methene-aniline dissolves in acids, not however forming salts with them, but being decomposed into aniline and diphenyl-ketone; the same result is produced when platonic chloride is added to its alcoholic solution; on the other hand, the hydrocarbon may be heated with water for ten hours without alteration.

Diphenyl-dichloromethane and *methyl-aniline* yield diphenyl-methene-aniline and dimethylaniline:



Ethylaniline acts in a similar manner, but *dimethylaniline* forms a base, $\text{C}^{12}\text{H}^{12}\text{N}$, the constitution of which may be either



its formation being represented by the equation



A small quantity of another base, $\text{C}^{12}\text{H}^{12}\text{N}_2$, is also formed at the same time. The compound $\text{C}^{12}\text{H}^{12}\text{N}$ forms salts with acids; its platino-chloride, $(\text{C}^{12}\text{H}^{12}\text{N.HCl})_2\text{PtCl}_4$, forms flattened yellow needles, slightly soluble in hot water, somewhat more in alcohol. The hydrochloride, nitrate, and sulphate are viscid oils, more soluble in alcohol than in water.

With *toluidine*, diphenyl-dichloromethane forms in like manner diphenyl-methene-toluidine, $(\text{O}^6\text{H}_5)_2\text{C}=\text{N}(\text{C}^6\text{H}_4\text{CH}_3)$, a highly refractive liquid decomposed by acids into diphenyl-ketone and toluidine; and with *naphthylamine* it yields diphenyl-methene-naphthylamine, $(\text{C}^6\text{H}_5)_2\text{C}=\text{N}(\text{O}^{10}\text{H}_7)$, crystallising in golden-

yellow rhombic plates, and decomposed by acids into diphenyl-ketone and naphthylamine.

Diphenyl-dichloromethane is not acted upon by ammonia in ethereal solution even in sealed tubes at 130°, but with alcoholic ammonia it yields diphenyl-ketone and ethylamine:—



Diphenyl-ketone itself is not acted on by ammonia, even in absolute alcoholic solution at 200° (Pauly).

Disulphochlorophenyl-dichloromethane, $\text{C}_6\text{H}_4\text{SO}_2\text{Cl}-\text{CCl}_2-\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$, also called *sulphochlorobenzophenonic chloride* and *benzophenone-disulphotetrachloride*, is formed by heating disulphodichlorophenyl-ketone (p. 682), with 4 mols. PCl_5 , to the melting point of the latter. The product poured into ice-cold water, washed, and treated with carbon sulphide, separates into two portions, viz., the unaltered ketone insoluble in the carbon sulphide, and disulphochlorophenyl-dichloromethane soluble therein. On evaporating to dryness and washing the residue with ether and alcohol, the latter compound remains as a white amorphous substance melting at 128°–129°, much less soluble in water and alcohol than the ketone from which it is formed, but almost equally soluble in chloroform (Beckmann, *Ber.* viii. 992).

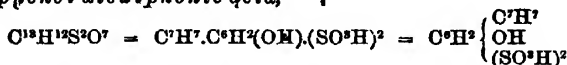
Hydroxydiphenyl-methane, or **Benzyl-phenol**, $\text{C}_6\text{H}_5\text{O}=\text{C}_6\text{H}_4\text{OH}=\text{C}_6\text{H}_4\text{OH}\cdot\text{C}_6\text{H}_4\text{OH}$ (Paternò, *Gazz. chim. ital.* ii. 1; Paternò a. Fileti, *ibid.* iii. 121, 251). This compound is formed by heating phenol with benzyl chloride and zinc. On distilling the product, unaltered phenol and benzyl chloride pass over below 260°, and on distilling the residue under diminished pressure (6 mm.), the greater part of it goes over between 180° and 190°, and solidifies on cooling to a crystalline mass of small needles, contaminated with an oil which may be removed by pressure and crystallisation from alcohol.

Benzyl-phenol crystallises in white silky needles or shining laminae, which are permanent in the air, and dissolve in ether, benzene, and chloroform. It melts at 84°, and boils under a pressure of 4–5 mm. at 175°–180°. It dissolves in alkaline liquids and is precipitated therefrom by acids; does not dissolve in ammonia. Nitric acid converts it into a nitro-derivative. Treated in acetic acid solution with bromine, it yields an unstable oily compound; but when dissolved in carbon sulphide and treated with excess of bromine, it yields a solid bromo-compound melting at about 175°, probably a dibromide. By the action of carbon dioxide and sodium at 150°, it is converted into benzyl-oxybenzoic acid, $\text{C}_6\text{H}_5\text{O}_2$ (p. 320).

The higher-boiling portions of the product obtained by the action of benzyl chloride on phenol in presence of zinc, contain anthracene and toluene. The anthracene is most probably formed, not by the action of the zinc on the benzyl chloride, but from the benzyl-phenol itself. This view is confirmed by the fact that when benzyl-phenol is distilled with its own weight of phosphoric anhydride, it yields a brown oily distillate, consisting almost entirely of benzene, phenol, and anthracene, the latter being formed by the reaction



Benzyl-phenol-disulphonic acid,



is formed by heating benzyl-phenol to 100° for about an hour with 1½ pts. of sulphuric acid. The phenol then dissolves completely, forming a brown liquid which when largely diluted with water, neutralised with lead carbonate, and filtered, leaves, on evaporation, a viscous substance which after a while solidifies to a white granular mass consisting of *benzyl-phenoldisulphonate of lead*, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\text{OH}\cdot(\text{SO}_3)_2\text{Pb}$. The acid liberated from this salt by hydrogen sulphide is uncrystallisable, so likewise are the ammonium, barium, and copper salts, the last of which is an amorphous chocolate-coloured substance; they are all soluble in water.

Benzyl-phenyl Acetate, $\text{C}_6\text{H}_5-\text{C}_6\text{H}_4-\text{OCH}_2\text{CO}$, is formed by the action of acetyl chloride at ordinary temperatures on benzyl-phenol. The mixture, after being heated for a short time to complete the reaction, is submitted to fractional distillation, the portion boiling between 310°–320° being collected apart. Another distillation renders the compound pure. It is a pale yellow liquid, with a slightly acetous odour, and of high refractive power. It boils at 317°, and has a density of 1.1043 at 16°. Exposed to the air, it absorbs moisture, and becomes decomposed, the reproduced benzyl-phenol crystallising out in fine needles. Heated with alcohol in a closed tube, it yields ethyl acetate and benzyl-phenol; with ammonia, acetamide is produced.

the oil which is formed as a secondary product in the preparation of benzyl-phenol.

Benzyl-phenyl Benzoate, $\text{C}^6\text{H}_5\text{—C}^6\text{H}_4\text{—OC}^6\text{H}_5\text{O}$, is formed in like manner by the action of benzoyl chloride on benzyl-phenol.³ It is very soluble in benzene, and separates therefrom in friable crystals belonging to the triclinic system; from alcohol it crystallises in thin plates and glistening needles. It melts at 86° , and is not decomposed by boiling alcohol or water, or by aqueous solution of potassium hydroxide. Heated with alcohol, however, in closed tubes to 100° , it is partially decomposed, with formation of ethyl benzoate.

Orthophosphate, $\text{PO}(\text{O.C}^6\text{H}_4\text{C}^6\text{H}_5)^3$, is formed by treating benzyl-phenol with phosphorus pentachloride. The two substances act violently on each other, with evolution of hydrochloric acid; and, on adding water to the product to decompose the excess of pentachloride, a brown oil is obtained, which solidifies on standing. This product, thoroughly washed with ether and recrystallised from chloroform, exhibits the composition of the orthophosphate. It forms colourless needles melting at $93^\circ\text{--}94^\circ$. It is decomposed by alcoholic potash, with formation of potassium phosphate and benzyl-phenol. Simultaneously with the phosphate, an oily compound, soluble in ether, is formed, which is believed to have the composition, $\text{C}^6\text{H}_5\text{.CH}^2\text{C}^6\text{H}_4\text{Cl}$.

³ } See the next article.

$\text{C}^{12}\text{H}^{10} = \text{CH}^2(\text{C}^6\text{H}_4\text{C}^6\text{H}_5)^2$ (J. Weiler, *Deut. Chem. Ges. Ber.* vii. 1188). This hydrocarbon is prepared by dissolving 15 grams of diphenyl and 5 grams of methylal in 250 grams of glacial acetic acid; adding a small quantity of a mixture of glacial acetic acid and sulphuric acid in equal volumes, to set up the reaction, and leaving the liquid to itself for twenty-four hours; then in the course of a day, adding by small portions 100 grams of glacial acetic acid and 100 grams of sulphuric acid; and, after another interval of 12 hours, adding 200 grams more of sulphuric acid. The whole is then poured into water, and the liquid thereby separated is distilled, whereupon unaltered diphenyl passes over first, after which the temperature rises quickly above 360° , and the diphenyl-phenyl-methane passes over. It is purified by solution in benzene, from which it separates by spontaneous evaporation in small colourless shining monoclinic crystals, melting at 162° .

Diphenyl-phenyl-methane is insoluble in water, but dissolves easily in benzene, chloroform, and acetone, less easily in glacial acetic acid, very sparingly in absolute alcohol. It dissolves in fuming sulphuric acid, forming a greenish-blue solution of a sulphonic acid which is decolorised by water. It dissolves also in fuming nitric acid, even at ordinary temperatures. It does not unite with picric acid.

Diphenyl-phenyl-ketone or diphenyl-benzophenone, $\text{CO}(\text{C}^6\text{H}_4\text{C}^6\text{H}_5)^2$, formed by boiling diphenyl-phenyl-methane with chromic acid mixture, shows very little tendency to crystallise, usually separating from its solutions in granular masses; once, however, it was obtained by crystallisation from acetone in tufts of small needles. It is insoluble in water, easily soluble in benzene, acetone, and glacial acetic acid; melts at 226° .

Diphenyl-phenyl-carbinol or diphenyl-benzhydrol, $\text{C}^{12}\text{H}^{10}\text{O} = \text{CHOH}(\text{C}^6\text{H}_4\text{C}^6\text{H}_5)^2$, formed by the action of sodium-amalgam on the ketone, crystallises in small white needles melting at 151° , and dissolving with extraordinary facility in alcohol and in benzene (Weiler).

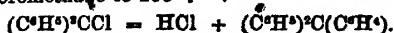
Diphenyl-methylphenyl-methane, $\text{CH}\left\{\begin{smallmatrix} \text{C}^6\text{H}_4 \\ \text{C}^6\text{H}_4\text{CH}^2 \end{smallmatrix}\right.$, is readily formed by boiling benzhydrol and toluene with phosphoric anhydride. It is an oily liquid having a peculiar odour, boiling at a very high temperature, and not solidifying in a freezing mixture.

Chromic acid oxidises it to an oxy-acid, $\text{C}^6\text{H}_4\text{C}^6\text{H}_4\text{C}^6\text{H}_4\text{O} < \text{C}^6\text{H}_4\text{—COOH}$, which may be obtained as a white powder by boiling the product of the reaction with a large quantity of baryta-water, and decomposing the barium salt with hydrochloric acid. It is insoluble in water, easily soluble in alcohol, ether, and light petroleum; crystallises with difficulty in indistinct needles; melts at 187° , and decomposes at a higher temperature.

The potassium and sodium salts are very soluble in water and in alcohol, and separate from the solutions on evaporation as heavy oils which gradually crystallise. The barium salt, $(\text{C}^{12}\text{H}^{10}\text{O})^2\text{Ba} + 7\text{H}_2\text{O}$, separates by slow cooling from its solution

(freed from excess of baryta by carbonic acid) in tufts of silky needles an inch long. It is very slightly soluble in cold water, and gives off its water of crystallisation over sulphuric acid (Hemilian, *Deut. Chem. Ges. Ber.* vii. 1299).

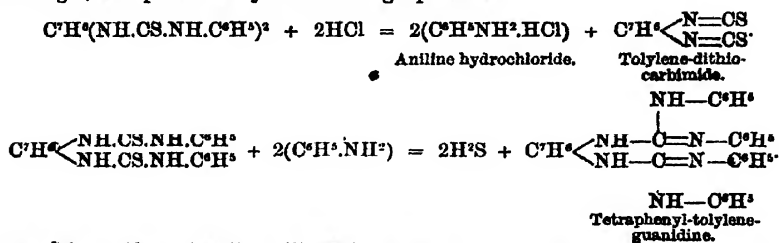
DIPHENYL-PHENYLENE-METHANE, $(C^6H^5)_3C(C^6H^5)$, is formed by heating triphenyl-chloromethane to 200° : π



It is somewhat sparingly soluble in ether and cold alcohol, easily soluble in hot alcohol and boiling glacial acetic acid, from which it crystallises in felted slender needles having a silky lustre. It melts at 188° , and distils undecomposed at a very high temperature (Hemilian, *loc. cit.*)

DIPHENYL-THIOCARBAMIDE, $OS(NH.C^6H^5)_2$. See CARBAMIDES, THIO- (p. 396).

DIPHENYL-TOLYLENE-DITHIOCARBAMIDE, $C^6H^5(NH.OS.NH.C^6H^5)_2$, separates after some time from an ethereal solution of tolylene-diamine and phenyl-thiocarbimide, as a white crystalline powder melting at 288° . Concentrated hydrochloric acid converts it into tolylene-dithiocarbimide, $C^6H^5(N=CS)_2$, and hydrochloride of tetraphenyl-tolylene-guanidine, the reaction apparently taking place by two stages, as represented by the following equations:



(Lussy, *Deut. Chem. Ges. Ber.* viii. 670).

DIPHENYL-TRICHLOROBUTANE, $C^6H^5Cl^2 = C^6H^5Cl^2-CH(C^6H^5)_2 = CCl^2-CH^2-CH^2-CH(C^6H^5)_2$ (E., Hepp, *Deut. Chem. Ges. Ber.* vii. 1611). This compound is prepared by treating a mixture of 4 pts. benzene and 5 pts. butyric chloral hydrate, with about three times its volume of a mixture of equal parts of ordinary and fuming sulphuric acid. The mixture is left to itself for a day, then poured into water, and the product, freed from undecomposed butyric chloral by washing with hot water, is crystallised from ether-alcohol with addition of animal charcoal.

Diphenyl-trichlorobutane crystallises from ether-alcohol in colourless monoclinic prisms half an inch long. Axial ratio, a (clinod.) : b (orthod.) = 1.0865 : 1. Angle, $ac = 120^\circ 8'7''$. Combination, $\infty P. \infty R \infty .0P$. The plane of the optic axes is the plane of symmetry; the angle between these axes is acute, and the first median line is nearly parallel to the principal crystallographic axis. The compound melts at 80° , and decomposes at higher temperatures, with evolution of hydrochloric acid. It dissolves at 25° in 2 pts. ether* and 48 pts. absolute alcohol, easily also in hot alcohol, acetone, chloroform, benzene, and carbon sulphide. The *dinitro-derivative*, $C^6H^5Cl^2(NO_2)_2$, crystallises from alcohol in small yellow tables, sparingly soluble in carbon sulphide and cold alcohol, easily in ether, chloroform, and benzene.

Diphenyl-trichlorobutane, heated with fuming sulphuric acid, yields a sulphonic acid whose barium salt, $C^6H^5Cl^2S^2O^6Ba$, is precipitated from its aqueous solution by alcohol.

$(C^6H^5)_2N-CO-OC^6H^5$, is formed by the action of ethylchlorocarbonate on diphenylamine dissolved in benzene. It is best crystallised from amyl alcohol, and when pure, crystallises in beautiful prisms. It melts at first at 72° , but, after prolonged heating, the melting point falls to 66° (Merz a. Weith, *Ber.* vii. 1611).

DIPHOSPHOBENZENE, $C^6H^5P^2OH = C^6H^5-P=P-OH$. This compound, the analogue of diazobenzene, is obtained by adding water, or better, alcohol, to the thick yellow liquid produced on passing dried spontaneously inflammable phosphoretted hydrogen through phosphenyl chloride. It is a powder which has a fine yellow colour,

* In Hepp's memoir this compound is regarded as diphenyl-trichlorobutylene, $CCl^2-CH=CH-CH(C^6H^5)_2$, and said to be formed from benzene and 'crotonic chloral,' $C^6H^5CH^2O$; but, as this latter has been shown to be really butyric chloral, $C^6H^5CH^2O$ (p. 443), the diphenylated compound formed from it is doubtless diphenyl-trichlorobutane.

is insoluble in water, slightly soluble in alcohol, easily in carbon sulphide; takes fire when heated in the air. Heated with nitric acid, it oxidises to a deep yellow liquid, which gradually becomes colourless, and then contains phosphoric as well as phosphenylic acid. On distilling the yellow liquid before the diphosphobenzene has separated from it, phosphenyl chloride escapes and a substance having a fine red colour remains behind (Michaelis, *Deut. Chem. Ges. Ber.* viii. 499).

DIPETHALYL, $C^6H^4O^2 - C^6H^4 \begin{smallmatrix} \diagup CO - CO \diagdown \\ \diagdown CO - CO \diagup \end{smallmatrix} O^2H^4$. This compound, treated with hydriodic acid and phosphorus, yields, as chief product, a bibasic acid, $C^6H^4O^4$ (Graebe, *ibid.* 1054).

DIPICRYLAMINE, $NH[C^6H^4(NO_2)^3]$. See BENZENES, NITRAMIDO- (p. 199).

DIPROPARGYL, $C^2H^3 = \begin{smallmatrix} H^2C - C \equiv CH \\ | \\ H^2C - C \equiv CH \end{smallmatrix}$. See PROPARGYL (2nd Suppl. 1008).

DIPROPYLCARBOBENZONIC ACID, $C^{20}H^{22}O^2$. An acid formed by the action of a solution of potassium hydroxide in normal propyl alcohol on deoxybenzoïn (p. 628).

DIPROPYLENE. See PROPYLENE.

DIPROPYLPHOSPHINE. See PHOSPHINES.

DIPSEUDOCUMENESULPHAMIDE, $NH(C^8H^{11}SO^2)$. See PSEUDOCUMENE-DERIVATIVES under TRIMETHYLBENZENE.

DIPSEUDOPROPYL KETONE. See PROPYL KETONES.

DIPSEUDOTOLYL-CARBAMIDE. See DITOLYL-COMPOUNDS.

DIPTEROCARPUS BALSAM or **GURJON BALSAM**. The volatile oil of this balsam, called *Wood-oil*, may be distinguished by the splendid violet colour produced on dissolving it in about 20 parts of carbon sulphide, and adding a drop of a cooled mixture of strong sulphuric and nitric acids. The same reaction is exhibited by the balsam itself, and is not interfered with by the presence of copaiba balsam. Cod-liver oil and valerian oil, similarly treated, likewise exhibit a fine violet colour, but for a short time only (Flückiger, *Pharm. J. Trans.* [3], vii. 2).

DI-RESORCIN. See RESORCIN.

DISSOCIATION. See HEAT, DECOMPOSITION BY.

DISTILLATION. Modifications of Linnemann's apparatus for fractional distillation (2nd Suppl. 436) have been devised by Le Bel a. Henniger (*Deut. Chem. Ges. Ber.* vii. 1084) with the view of accelerating the condensation, obviating the necessity of constant watching, and effecting a more complete separation of the mixed liquids.

The apparatus of Le Bel a. Henniger (fig. 1) consists of a long glass tube with a number of bulbs blown on it, wider than those in Linnemann's apparatus, and having a contraction below each bulb for the purpose of hindering the downward flow of the liquid and causing it to collect in the bulb; the passage may, if necessary, be still further narrowed by the introduction of small fragments of glass, or better, of little balls of platinum wire. The back-flow of the condensed liquid into the distilling vessel is effected by means of narrow tubes, *a*, *b*, fused into the wide tube and bent so as to prevent the vapours from passing upwards through them. These tubes must be long enough to prevent the liquid from being thrown out by the pressure existing in the boiler and the bulbs. The number and size of the bulbs depend, of course, upon the quantity of liquid to be distilled, and the more or less complete separation to be effected. The figure represents an apparatus with two bulbs for the distillation of about 500 c.c. of liquid. Two such tubes may be easily arranged one above the other and connected by corks, caoutchouc, &c.

Commercial wood-spirit, distilled in an apparatus of this kind with five large bulbs, yielded, after two distillations, two-thirds of its bulk of acetone boiling between 56° and 58° , three litres of distillate being collected in about six hours.

Glinky's apparatus (fig. 2) is provided, like that of Linnemann, with cups of platinum wire-gauze, but differs from the latter in having larger bulbs and a bent lateral tube for the back-flow of the condensed liquid. The following are the dimensions recommended for distilling various quantities of liquid of different degrees of volatility.

1. For distilling large quantities of liquid of boiling point not above 150° , the tube should be 50 cm. long, 2 cm. in diameter, and provided with five platinum-gauze cups; diameter of the capillary aperture in the lateral tube = 1 mm.

2. For distilling from $\frac{1}{2}$ to 5 kilo. of liquid boiling below 160° , the principal tube

should be 40 cm. long, 12 to 13 mm. wide, and provided with five to six platinum-gauze cups: diameter of capillary aperture in lateral tube = $\frac{1}{4}$ to $\frac{1}{2}$ mm.

3. For distilling 100 to 500 grams of liquid boiling not above 200°, the principal

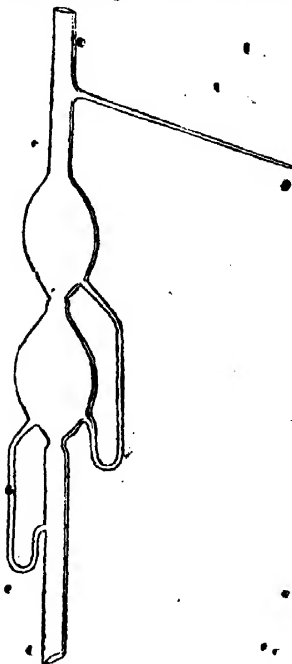


FIG. 1.

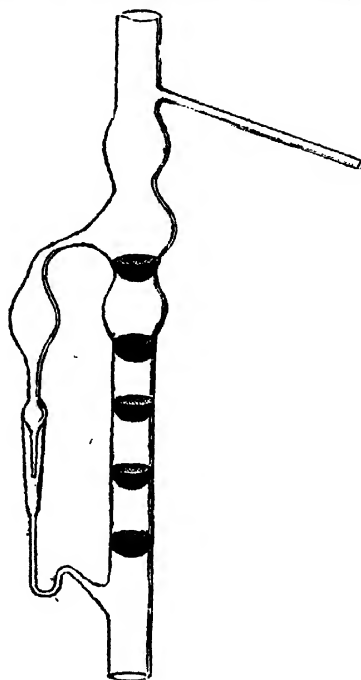


FIG. 2.

tube should be half as long and half as wide as the last, and the diameter of the capillary aperture in the lateral tube 1 mm.

DITA BARK (J. Jobst and O. Hesse, *Liebigs Annalen*, clxxviii, 49-79). Dita is the name given by the inhabitants of the Philippines to the bark of *Echites scholaris* (a), the *Alstonia scholaris* of Brown, a forest-tree belonging to the natural order Apocynaceæ. Gruppe, an apothecary at Manilla, first isolated from this bark a substance which he called *Ditain*, possessing febrifugal properties. Gorup-Besanez (*ibid.* clxxvi. 88) afterwards extracted from ditain a crystallisable substance which proved to be an alkaloid, but which, for want of material, he did not completely examine.

Dita bark usually consists of irregular curved fragments from 40 to 60 mm. long, 15 mm. wide and 1 mm. thick, covered externally with a thin leather-coloured cortical layer, and often exhibiting transverse and longitudinal furrows. The inner surface is slightly reticulated and longitudinally striated. The bark is moderately hard and easily friable, yielding a yellowish-grey powder, which is scentless, and produces, after some time only, a bitter but not unpleasant taste. Under the microscope, the cells of the bark are seen to contain crystalline deposits, probably consisting of calcium oxalate.

The following definite principles have been extracted from the bark :

1. **Ditamine** or **Ditaine**, the alkaloid of the bark, is best extracted by boiling alcohol after the bark has been freed from fatty matter by means of light petroleum. The alcohol after distillation leaves a solution containing a salt of ditamine, which may be decomposed by addition of soda, and the base may be removed by agitation with ether. The ethereal solution shaken with weak acetic acid gives a solution which, after decolorising with animal charcoal, yields, on addition of ammonia, a white amorphous precipitate of the alkaloid amounting to about .02 per cent. of the bark.

Ditamine is easily soluble in ether, chloroform, benzene, and alcohol, and on

evaporation remains in the form of an amorphous mass. It sometimes seemed to crystallise from petroleum spirit. It melts at 75° .

Its salts are generally amorphous, but the hydrochloride was once obtained in the form of needles. The hydrochloride gives with platonic chloride a yellow amorphous precipitate, besides precipitates with gold chloride, mercuric chloride, and mercuric iodide dissolved in iodide of potassium. Precipitates are also obtained with iodide of potassium, thiocyanate of potassium, tannin, and phosphomolybdic acid, but no change occurs on addition of ferric chloride. The base has not been analysed, the quantity obtained not being sufficient for the purpose.

2. Echicaoutchin. This substance, together with those which follow, is extracted from the bark by treatment with light petroleum as above mentioned. On expelling the petroleum from the extract by boiling with water, there remains a gelatinous ropy mass which hardens on cooling, and may then be easily broken into lumps. This mass is repeatedly treated with boiling alcohol till a portion of the alcohol taken out no longer deposits crystals on cooling, but merely becomes milky. There then remains an extremely elastic residue which dissolves in petroleum, forming a milky solution which cannot be clarified by filtration, but only by leaving it at rest for several months till the suspended matter has settled down, or by distilling off the petroleum and heating the remaining liquid to about 100° , whereby the finely divided suspended matter appears to be coagulated into denser masses. On repeatedly treating this residue with cold petroleum, the echicaoutchin is dissolved and white flocks remain, consisting of a kneadable resin which melts above 100° , is nearly insoluble in ether and light petroleum, but dissolves sparingly in boiling alcohol and very easily in chloroform. A clear solution having been thus obtained, it is next treated with animal charcoal, which nearly removes the yellow colour; the petroleum is evaporated off, and the residue is repeatedly treated first with boiling alcohol and then with hot water.

Echicaoutchin thus obtained has the composition $C^{20}H^{40}O^2$. It is a tough yellow body, brittle below 0° , but softens when immersed in lukewarm water, and may then be drawn out into silky threads. It dissolves easily in chloroform, ether, benzene, and light petroleum, but hot alcohol dissolves only traces of it. It is insoluble in strong potash-ley, oxidised to a yellow mass by strong nitric acid, blackened in the cold by strong sulphuric acid, resolved into small particles when heated therewith. Bromine added to its solution in chloroform blackens the liquid and appears to decompose the echicaoutchin.

3. Echicerin, $C^{20}H^{40}O^2$. When the petroleum extract of the bark is boiled with hot alcohol, the alcoholic solution, on cooling, first deposits an oily mass which afterwards solidifies, and then a considerable quantity of white crystals, an additional quantity of which may be obtained by dissolving the solidified mass above mentioned in hot acetone and leaving the solution to cool. The crystals thus obtained are a mixture of echicerin and echitin, which may be separated by drenching the mixture with a quantity of light petroleum sufficient to make it into a stiff pulp, and after a while pouring off the liquid portion, which contains chiefly the echicerin. The petroleum is then expelled by heat, and the residue dissolved in boiling alcohol, which on cooling deposits the echicerin still mixed with small quantities of echitin, to be separated by repeated crystallisation from boiling alcohol.

Echicerin crystallises from boiling alcohol in stellate or nodular groups of small anhydrous needles. It is very slightly soluble in cold alcohol, but dissolves with extreme facility in ether, light petroleum, acetic ether, benzene, and chloroform, less easily in acetone, and is insoluble in water, potash, ammonia, and dilute acids.

Echicerin turns the plane of polarisation to the right, its specific rotatory power is in ethereal solution $\alpha_D = +63.75^{\circ}$; in chloroform solution $+65.75^{\circ}$. It melts at 157° , and at higher temperatures creeps up the sides of the vessel without actually distilling, emitting at the same time a faint odour like that of heated caoutchouc.

Bromechicerin, $C^{20}H^{40}BrO^2$, is formed by dropping bromine dissolved in chloroform into a chloroform solution of echicerin. The resulting solution is left to evaporate in the air; the residue is melted in boiling water to remove hydrobromic acid; and the bromechicerin thus obtained is purified by crystallisation from boiling alcohol, which dissolves it with moderate facility, and deposits it on cooling in dull white or sometimes transparent spherules gradually becoming crystalline. It dissolves readily in chloroform and light petroleum; does not unite either with bases or with acids, or with water. When triturated it yields a white powder melting at 116° .

Echiceric acid, $C^{20}H^{40}O^4$, is formed by adding sodium to a solution of echicerin in petroleum (b. p. about 80°) and heating the mixture to 60° from time to time. After this treatment had been continued for about two months, the solution, containing caustic soda formed by oxidation of the sodium, was decanted from a fatty deposit

(probably impure echicerin) and supersaturated with hydrochloric acid, and the echiceric acid thereby liberated was dissolved in ether, which left it on evaporation as an amorphous mass.

Echiceric acid is inodorous, melts at a little below 160° , is easily soluble with acid reaction in alcohol, soluble also in ether and in chloroform. It dissolves in alkalis, and the ammoniacal solution, containing excess of echiceric acid, gives white precipitates with barium chloride, silver nitrate, and lead acetate.

Just a. Hesse represent the formation of echiceric acid from echicerin by the equation :



4. **Echitin**, $C^{22}H^{32}O^2$, remains for the most part undissolved when the mixture already mentioned (p. 688) is treated with petroleum; and on dissolving this residue in boiling alcohol, and leaving the solution to cool, echitin separates out first, and then, after some hours, a small quantity of echicerin. By one more crystallisation from alcohol the echitin is obtained pure.

Echitin forms white anhydrous scales which melt at 170° , and require 1480 parts of 80 per cent. alcohol at 15° for solution. Its solution in ether has a right-handed rotation $[\alpha]_D = +72.72^{\circ}$. In chloroform $[\alpha]_D = +75.25^{\circ}$.

This compound is indifferent to acids and bases, but forms with bromine a well characterised substitution-product, $C^{22}H^{31}BrO^2$, which is obtained in the same manner as bromechicerin, and separates from boiling alcohol in colourless gelatinous spherical masses, gradually becoming hard and crystalline. It melts without loss at 100° , dissolves easily in ether, chloroform, and benzene, has a neutral reaction, and is altogether an indifferent substance.

5. **Echiteïn**, $C^{22}H^{30}O^2$, remains partly in the alcoholic solution from which the mixture of echicerin and echitin has separated, partly in the oily mass which separates from the solution in the first instance (p. 689). When the alcoholic mother-liquor is left to evaporate at 40° – 50° , the sides of the vessel soon become clothed with delicate arborescent crystals of echiteïn, in the midst of which a viscid fluid mass gradually collects. The crystals are separated from this substance by filtration at the same temperature, and finally by pressure between filter-paper. A portion of the echiteïn is, however, contained in the viscid liquid, and may be separated by dissolving the whole in hot acetone and leaving the solution to crystallise in tall vessels; it then deposits frosty, heavy, nodular, crystalline groups of echicerin and echitin, afterwards light needles of echiteïn, and lastly a resinous substance called *echiretin*. The echiteïn is easily separated from the heavier crystals of echicerin and echitin by levigation with the mother-liquor before the separation of the resinous echiretin begins. Lastly, the two portions of crude echiteïn, obtained as above, are stirred up with a small quantity of light petroleum, the liquid is pipetted off, and echiteïn, purified by recrystallisation from boiling alcohol.

Echiteïn crystallises from hot strong alcohol in light needles, which consist of prisms apparently belonging to the rhombic system. 1 pt. dissolves in 960 pts. of 80 per cent. alcohol at 15° . Right-handed rotation, $[\alpha]_D = 88^{\circ}$ in ether; 85.45° in chloroform. It melts at 195° , forming a colourless liquid which crystallises at 168° .

Bromechiteïn, $C^{22}H^{30}BrO^2$, prepared like the brominated derivatives of echicerin and echitin, forms, when dry, a yellow powder melting at 150° , easily soluble in boiling, less easily in cold alcohol. Chloroform and ether dissolve it readily, and leave it on evaporation as a gelatinous mass in which crystals afterwards form. It is not attacked by potash, but dissolves with purple-red colour in strong sulphuric acid.

6. **Echiretin**, $C^{32}H^{46}O^2$. After the greater part of the echiteïn has crystallised out from the alcoholic or acetonic solution, as above described, a yellowish-green oil begins to separate, which is a solution of echiretin in alcohol or acetone; and on dissolving this oil in acetone, and leaving the solution to evaporate in a tap-funnel, the echiretin gradually collects in the tube of the funnel as an oil mixed with crystals of echiteïn. On opening the tap, this oil, together with some of the acetonic solution, runs off, while the crystals of echiteïn are retained. The oily layer of echiretin is then separated by a pipette, dissolved in ether, and decolorised by animal charcoal. After the evaporation of the ether, the echiretin remains as a yellowish very brittle residue, easily separated from the sides of the vessel.

Echiretin forms a translucent mass which may be rubbed down to a white powder. It is tasteless, neutral to test-papers, and melts at 52° . It dissolves easily in ether, light petroleum, chloroform, boiling acetone, and boiling alcohol, and separates from the last two solutions, when sufficiently concentrated, in the form of an oil. Rotatory power in ethereal solution, $\alpha = +54.82^{\circ}$. Bromine is easily absorbed by it. Strong nitric acid converts it into a yellow easily fusible resin. Strong sulphuric acid dissolves it

at ordinary temperatures, forming a blood-red solution, which becomes brown-red when heated.

A comparison of the formulae of these resinoid substances seems to indicate that they have a close relationship to one another, and to the similar compounds obtained from the milky juice of other plants.

Echicaoutchin	$(C^6H^4)^2O^2$
Echicerin	$(C^6H^4)^2O^2$
Echiretin	$(C^6H^4)^2O^2$

Echitin is also homologous with echicerin, and echiteïn with echiretin:

Echicerin	$C^{10}H^{14}O^2$	} Difference C^2H^4
Echitin	$C^{12}H^{16}O^2$	
Echiretin	$C^{10}H^{14}O^2$	} Difference C^2H^{14}
Echiteïn	$C^{12}H^{16}O^2$	

Echiretin and echicerin are probably identical with two resins obtained by Heints from the milk of the Cow-tree (*Tabernamontana utilis*).

Echigerin also has the same percentage composition as lactucerin, although the properties of the two bodies do not agree in every respect. Cubob camphor is another body which appears to be isomeric with echicerin, whilst the antiaretin obtained by de Vrij and Ludwig from the *Antiaris toxicaria* seems to agree with echiteïn.

Dita bark contains, in addition to the substances above described, a small quantity of another alkaloid, soluble in water and alkalis, but insoluble in ether. Jobst a. Hesse are, however, of opinion, that this bark will never become a productive source of crystallisable alkaloids, and that its febrifuge qualities, if it possesses any, must be due to some of the other constituents.

The bark also yields calcium oxalate, and some acids precipitable by acetate of lead.

DITARTARIC ACID. See TARTARIC ACID.

DITHIOBENZOIC ACID. See BENZOIC ACID DERIVATIVES (p. 297).

DITHIOCYANIC ACID. See CYANIC ACID (DITHIO-) (p. 608).

DITHIONIC ACID. See SULPHUR ACIDS OF OXYGEN.

DITHIOPRUSSIANIC ACIDS. See THIOPRUSSIANIC ACIDS.

DITETRAOXYLETHANE. See DIOXYTETRAETHANE (p. 656).

DITOLYL, $C^6H^4-CH^3$ $\left| \begin{array}{l} C^6H^4-CH^3 \\ C^6H^4-CH^3 \end{array} \right.$ *Di-methyl-phenyl*.—Solid ditolyl, prepared by

the action of sodium on parabromotoluene (2nd Suppl. 1179), is not altered by heating to 500° for a quarter of an hour, but by longer heating it is decomposed, with separation of charcoal; no anthracene or phenanthrene is formed in this decomposition. Liquid ditolyl (b.p. 280°–285°) from the same source is completely resolved by heating for five minutes into anthracene (with a small quantity of phenanthrene), toluene, and free hydrogen, $2C^6H^4-CH^3 = C^{14}H^{18} + 2C^6H^5 + H^2$. A third modification (α -ditolyl), prepared from liquid bromotoluene, is resolved at 500°–600° into a mixture of phenanthrene, anthracene, and toluene [with evolution of hydrogen] (Barbier, *Compt. rend.* lxxviii. 1769; *Ann. Ch. Phys.* [6], vii. 615).

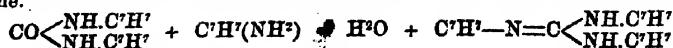
Solid ditolyl dissolved in acetic acid is oxidised by excess of chromic acid to diphenyldicarboxylic acid, $(C^6H^4)^2(COOH)^2$ (Doebner, p. 667).

By incomplete oxidation with 2.294 pts. CrO^3 to 1.117 of the hydrocarbon, solid ditolyl yields *tolyl-phenyl-carboxylic acid*, $CH^3.C^6H^4.C^6H^4.COOH$, melting at 243°–244°. Liquid ditolyl, m.p. 270°–280° and 280°–290°, oxidised with about three times its weight of CrO^3 , gives a *tolyl-phenyl-carboxylic acid* melting at 176°; with 7 pts. CrO^3 , a *diphenyl-dicarboxylic acid* isomeric with the one obtained from solid ditolyl; and with 11 pts. CrO^3 it is completely oxidised to *terephthalic acid*. Solid ditolyl appears to be the *para-para*- and liquid ditolyl the *ortho-para* modification of di-methylphenyl (Carnelly, *Chem. Soc. J.* 1877, ii. 653).

DITOLYLAMINE, $(C^6H^4)^2NH$, is formed by heating toluidine, $(C^6H^4)NH^2$, with its hydrochloride. It forms long white needles which melt at about 70°. *Acetyl-ditolylamine*, $(C^6H^4)^2N(C^2H^5O)$, boils at 85°; *benzoyl ditolylamine*, $(C^6H^4)^2N(C^6H^5O)$, boils at 125° (Gerber, *Deut. Chem. Ges. Ber.* vi. 446).

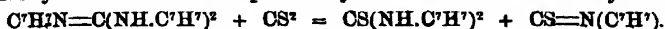
DIPSEUDOTOLYL-CARBAMIDE, $CO(NH.C^6H^4)^2$, prepared by heating pseudotoluidine (orthotoluidine) with urea, crystallises in white needles. Treated with carbon disulphide, it yields di-pseudotolyl-thiocarbamide and carbon oxysulphide, $CO(NH.C^6H^4)^2 + CS^2 = COS + CS(NH.C^6H^4)^2$. Heated

with phosphorus trichloride and pseudotoluidine, it is converted into tri-pseudotolyl-guanidine.



which is also formed from ditolyl-thiocarbamide by heating it with pseudotoluidine alone, or in alcoholic solution with pseudotoluidine and lead oxide.

Tri-pseudotolylguanidine heated to 180° with carbon disulphide is converted into di-pseudotolyl-thiocarbamide and pseudotolyl-thiocarbimide or isothiocyanate:



Pseudotolylthiocarbimide is, however, best obtained by boiling di-pseudotolylthiocarbamide with fuming hydrochloric acid:



It is a colourless, strongly refracting liquid having a pungent odour, easily volatilising with vapour of water, and boiling constantly at 239°. Like other thiocarbimides (mustard oils), it easily unites with amines to form thiocarbamides (thio-ureas) (E. Girard, *Deut. Chem. Ges. Ber.* vi. 444).

Ditolylcarbamide (m.p. 256°) and ditolylthiocarbamide (m.p. 176°) from paratoluidine have been already described (pp. 392, 398).

DITOLYL-ETHANE or **DIMETHYLPHENYLETHANE**, $(\text{C}^{\text{H}'}.\text{CH}^3)\text{HC}-\text{CH}^3$, is formed by the action of acetaldehyde on toluene. To prepare it, paraldehyde is added, slowly and with frequent agitation, to well-cooled sulphuric acid till the acid has dissolved from 1 to 1½ per cent. of it, after which toluene is gradually added in the proportion of 2 mol. $\text{C}^{\text{H}'}\text{H}^3$ to 1 mol. $\text{C}^{\text{H}'}\text{H}^3\text{O}$, rise of temperature being all the while carefully prevented by cooling with ice. The mass, after being well shaken and then left at rest for a few hours, is poured into a large quantity of water, and the oil which rises to the surface is removed and shaken with ether. A considerable quantity of resin formed at the same time must also be agitated with ether. On subjecting the ethereal solution to fractional distillation, dimethylphenylethane passes over at 295°–298°, and is easily obtained pure by drying it in contact with sodium. The quantity obtained is about equal to that of the aldehyde employed.

Ditolyl-ethane is a strongly refractive oil having a fragrant aromatic odour, and not solidifying at –20°. With cold fuming nitric acid, it yields a nitro-compound which forms small highly lustrous crystals. It also forms a substitution-compound with bromine. On passing its vapour through a red-hot tube, methyl-anthracene, $\text{C}^{10}\text{H}^{12}$, is formed. By oxidation with potassium dichromate and sulphuric acid, it yields the same products that Wieler obtained by the oxidation of ditolyl-methane (*q.v.*) viz. ditolyl-ketone (m.p. 94°), and tolylbenzoic acid, $\text{CO} \begin{array}{c} \text{C}^{\text{H}'}-\text{CH}^3 \\ \text{C}^{\text{H}'}-\text{CO}^2\text{H} \end{array}$ (m.p. 222°) (O. Fischer, *Deut. Chem. Ges. Ber.* vii. 1191).

Ditolyl-monochlorethane, $(\text{C}^{\text{H}'}.\text{CH}^3)\text{HC}-\text{CH}^2\text{Cl}$, prepared from monochloraldehyde and toluene, in the same manner as diphenylmonochlorethane from monochloraldehyde and benzene (p. 674), is resolved by distillation into hydrochloric acid and dimethyl-stilbene, $(\text{C}^{\text{H}'}.\text{CH}^3)^2\text{C}=\text{CH}^2$ (Happ, *ibid.* 1413).

Ditolyl-trichlorethane, $(\text{C}^{\text{H}'}.\text{CH}^3)\text{HC}-\text{CCl}_2$, is prepared by stirring a mixture of 1 mol. chloral and rather more than 2 mol. toluene into strong sulphuric acid. To the mixture, which becomes hot and acquires a dark red-brown colour, sulphuric acid is added in a cooled vessel till the whole becomes pasty, and the product, which quickly solidifies, is thrown into a large quantity of water, boiled with water for several hours, then dissolved in alcohol or ether-alcohol, and decolorised by animal charcoal.

Ditolyltrichlorethane forms fine crystals melting at 89°, and decomposing at a higher temperature. It dissolves in 2 pts. of ether and in 40 pts. of alcohol. Boiling alcoholic potash converts it into ditolyldichlorethane, $(\text{C}^{\text{H}'}.\text{CH}^3)_2\text{C}=\text{CCl}_2$, which crystallises in very brilliant needles melting at 92°, soluble in 2 pts. ether and 36 alcohol.

Dinitroditolyl-trichlorethane, $\text{C}^{10}\text{H}^{10}\text{Cl}_3(\text{NO}^2)_2$, formed by dissolving the trichloro-compound in fuming nitric acid at the heat of the water-bath, crystallises in short brilliant yellowish prisms melting at 120°–122°.

Dibromoditolyl-trichlorethane, $\text{C}^{10}\text{H}^{10}\text{Cl}_3\text{Br}_2$, is formed by adding bromine (2Br^2) to a solution of ditolyl-trichlorethane in carbon disulphide; the action is completed in a few days. On evaporating the solvent and treating the residue with light petroleum, a white powder is obtained, which, by crystallisation from alcohol, is converted into shining iridescent laminae. The compound melts at 148°, and gives up 1 mol. HCl when treated with potash.

Carboxylphenyl-tolyl-trichlorethane, $C^{16}H^{11}Cl^3O^2 = CCl^3-CH \begin{smallmatrix} C^6H^4-CO^2H \\ C^6H^4-OH^2 \end{smallmatrix}$

is formed by boiling ditolyl-trichlorethane for five or six days with chromic acid mixture. A solid mass then separates out, which must be exhausted with boiling ammonium carbonate, and the resulting solution treated with hydrochloric acid yields a precipitate of the carboxyl-compound. Strong alkalis must not be used for the exhaustion of the crude product, as they would abstract hydrochloric acid and produce a mixture of the compounds, $C^{16}H^{11}Cl^3O^2$ and $C^{16}H^{11}Cl^2O^3$, which would be difficult to separate.

Carboxylphenyl-tolyl-trichlorethane crystallises from glacial acetic acid and alcohol in tablets melting at $173^\circ-174^\circ$. It is a monobasic acid, and its alkali-salts crystallise well; the barium, calcium, and magnesium salts are flocculent sparingly soluble precipitates (Fischer).

See UREIDES.

DIXYLTL. See XYLYL.

DOLERITE. In support of his views respecting the relations of dolerite, anmesite, and basalt (2nd Suppl. 439), Sandberger has analysed some of the constituent minerals of the dolerite of the Frauenberg near Heubach. The results show that dolerite consists of andesin, titanic iron, augite, altered olivine, and apatite, whereas basalts are destitute of titanic iron, and probably contain labradorite instead of andesin. There are also basalts (e.g. those of Löwenburg in the Siebengebirge, and Oberbrechen in Nassau) which approach dolerite in their coarse-grained structure, though not in their mineralogical constitution (*Jahrb. f. Min.* 1874, 88).

From analyses by G. W. Hawes (*Sill. Am. J.* [3], ix. 185; *Chem. Soc. J.* 1876, i. 350), it appears that the trap-rock, which, in the form of dikes, intersects the mesozoic sandstone of the Connecticut valley, has, when unaltered, very nearly the composition of dolerite (see TRAP-ROCKS).

On the Microscopic Structure and Composition of British Carboniferous Dolerites, see S. Allport (*Geol. Soc. Qu. J.* xxx. 529; *Jahrb. f. Min.* 1876, 425).

DOLOMITE. *Formation.*—F. Hoppe-Seyler (*Zeitschr. Geol. Ges.* xxvii. 495) infers, from numerous experiments, that dolomite cannot have been formed at ordinary temperature. At higher temperatures, however, magnesium salts act upon lime in such a manner as to produce dolomite, the reaction commencing at temperatures a little above 100° : in this manner dolomite may be formed by the natural action of seawater, calcium carbonate, and carbonic acid. Haines & Doelter (*Jahrb. f. Min.* 1876, 310), from an examination of the dolomitic formations of South Tyrol, have arrived at results agreeing very well with those of Hoppe-Seyler (without reference to temperature). They conclude that slightly dolomitic limestone formations of great extent and thickness have been produced directly from marine organisms, and that normal dolomite, $CaCO^2.MgCO^2$, which occurs much less abundantly, has been formed by subsequent addition of magnesium. Dolomites rich in magnesium have for the most part been produced by the action of marine magnesium salts on calcium carbonate, and local differences of composition are due to the subsequent action of running water. For analyses of dolomites on which these conclusions are founded, see the memoir above cited; also *J. pr. Chem.* 1875, 1259. Hörnes (*Verhandl. geol. Reichsanst.* 1876, 76) disputes the conclusions of Hoppe-Seyler respecting the temperature at which dolomites have been formed, as inconsistent with observed geological relations, especially in South Tyrol.

Crystalline form.—The following axial relations of calcspar and dolomite have been deduced from very careful measurements by N. v. Kokscharow (*N. Petersb. Acad. Bull.* xxi. 47).

	Principal axis	Secondary axis	Angle of rhombohedron
• — Calcsp.	0.854628	: 1	$105^\circ 4' 0''$
Dolomite	0.831933	: 1	$106^\circ 16' 0''$

A white granular dolomite from Vigo in the Massathet, having very nearly the normal composition $CaO.CO^2 + MgO.CO^2$, has been analysed by J. Rumpf (*Min. Mittheil.* 1873, 33) with the following results: . . .

	CO ₂	CaO	MgO
Found	47.42	30.07	21.79 = 100.18
Calc.	47.53	30.43	21.74 = 100

C. A. Bart (*Sill. Am. J.* [3], vi. 213) has analysed a dolomite from the magnetic iron ore locality of the Tilly-Foster Mine, Putnam County, New York. The percentage composition is:

CO ²	CaO	MgO	MnO	FeO
46·97	30·30	20·78	0·13	0·91 = 99·06

whence may be deduced the following proportions of the carbonates :

CaCO ³	MgCO ³	FeCO ³	MnCO ³
53·82	43·66	1·13	0·63 = 99·24

Blue-grey *Wellendolomite*, from Ittersbach in Baden, used as a hydraulic lime, has been analysed by Brigel (*Jahresb. f. Chem.* 1873, 1228):

CaCO ³	MgCO ³	Al ² O ³	FeO	K ² O	Na ² O	K [*]
54·48	31·16	6·71	2·17	0·26	1·83	2·85 = 99·46

* Insoluble residue consisting of SiO², Al²O³, Fe²O³.

Vogelgesang (*Jahrb. f. Min.* 1873, 43) gives analyses by A. Mayer of two marly Wellendolomites from the Black Forest of Baden : 1. from Königsfeld; 2. from Mönchweiler; A. total analysis; B. portion soluble in hydrochloric acid.

	CO ²	P ² O ⁵	CaO	MgO	Na ² O	K ² O	Al ² O ³	Fe ² O ³	SiO ²	
1 A.	36·80	0·06	20·93	17·51	0·86	0·96	2·68	6·80	10·39	96·99
B.	36·80	—	20·68	17·35	0·50	0·12	trace	4·59	0·26	80·30
2 A.	11·20	0·12	16·56	4·64	0·65	1·96	21·77	44·18	= 101·08	
B.	11·20	—	16·20	1·00	0·23	0·53	0·14	1·14	0·18	= 30·62

The analyses include undetermined water and organic matter.

Other varieties of this rock, which is very generally used for marling the fields, exhibit a strong reaction of chlorine.

Mayer has also analysed a *Trigonodus dolomite* from Hüfingen in the Baden Black Forest, used for the preparation of hydraulic mortar :

CaCO ³	MgCO ³	Fe ² O ³	Al ² O ³	H ² O	Clay
46·35	28·35	1·70	—	2·45	19·60 = 98·45

In other localities, Franconia, for example, this rock is developed as a very pure limestone.

See COPPER ARSENIDES (2nd Suppl. 388).

DUALIN. An explosive material consisting of nitrated sawdust saturated with nitroglycerin.

DUDLEYITE. A new mineral from Dudleyville and the Cullakanee Mine in North Carolina, formed by the transformation of margarite, which occurs in its immediate neighbourhood. Colour bronze- to brown-yellow. Analysis gave

SiO ²	Al ² O ³	Fe ² O ³	FeO	MgO	Na ² O	K ² O	Li ² O	Loss by ignition
32·42	28·42	4·99	1·72	16·87	1·52	0·56	0·19	13·43 = 100·12

(F. A. Genth, *Jahrb. f. Chem.* 1873, 1155).

DUFRENOYSITE (ii. 347). R. W. E. Macivor (*Chem. News.* xxx. 103) has published an analysis of Swiss dufrenoyite, agreeing very nearly with that previously made by Stockar-Escher (ii. 347), and therefore corroborating the identity in chemical composition of monometric dufrenoyite and trimetric or rhombic enargite.

a. Direct results of Macivor's analysis : b. Analytical values after reduction of Ag to Cu : c. Calculated composition of enargite, Cu²As³S³ or 3Cu²S·As³S³.

	Cu	As	S
a (found)	46·05	2·43	18·79
b (corrected)	47·48	—	18·79
c (calculated)	48·29	—	19·10
			32·61 = 100

A dufrenoyite from the Binnenthal (vom Rath's binnite) with numerous faces, has been described by Hessenberg (*Jahrb. f. Min.* 1875, 646). It exhibits a rhombic character by distortion, and if all its faces were developed, would have 170. The faces 404, 10010, and 40 are described as new. It occurs in association with blende and galena.

DULCAMARIN. This name was given by Wittstein to a nitrogenous substance which he obtained from the stalks of *Solanum dulcamara* (ii. 346). This substance has been further examined by E. Geissler (*Arch. Pharm.* [3]. vii. 289), who, by treating it with ammonia, has freed it from a nitrogenous impurity, and by converting the remaining substance into a lead compound, and decomposing the latter with hydrogen sulphide, has obtained a pure non-azotised body having the composition C²²H²⁴O¹⁶. This dulcamarin is amorphous, tastes bitter at first, afterwards persistently sweet ;

dissolves in alcohol and acetic ether; and is precipitated by basic lead acetate, yielding the compounds $C^2H^2PbO^{10} + 3H^2O$ and $C^2H^2PbO^{10} + 5H^2O$.

By the action of dilute acids, dulcarnarin is resolved into glucose and a resinous compound $C^2H^2O^4$, called dulcamaretin.



DURANGITE. This fluorarsenate of aluminium and sodium, first recognised as a distinct species by Brush (*2nd Suppl.* 442), is found, together with topaz, in the stanniferous sands near Durango in Mexico, forming small isolated brittle crystals, nearly as hard as apatite, having a conchoidal fracture and orange-red colour, and yielding a yellow powder. The crystals are monoclinic, most frequently exhibiting the combinations $\infty P. + P$; $\infty P. + \frac{1}{2}P$; $\infty P. \infty P^{\infty} + P. \frac{1}{2}P$; and $\infty P. + P. - \frac{1}{2}P$. Besides these, Descloizeaux has observed a clinodome, $2R\infty$, and the clinopinacoid $\infty R\infty$; the basal face OP has not been observed. Angle, $\infty P = 110^{\circ} 10'$; $+ P = 112^{\circ} 10'$. Cleavage moderately distinct, prismatic. Hardness = 5. Sp. gr. = 3.95-4.03. Colour, light reddish-yellow. Lustre, strongly vitreous. The plane of the optic axes is perpendicular to the plane of symmetry. The first bisectrix of the optic axes is negative, and the angle between these axes is too large to allow both the ring-systems to be seen at once in air. In oil this angle is about $80^{\circ} 53'$ for red, and $80^{\circ} 49'$ for yellow rays; so that there is a slight dispersion $p < v$. Thin laminae exhibit the horizontal dispersion characteristic of the monoclinic system.

In chemical composition, durangite exhibits some analogy to amblygonite, but the latter is triclinic, and differs altogether from durangite in optical and physical characters (Descloizeaux, *Ann. Chim. Phys.* [5], iv. 401).

Brush (*Sill. J.* [3], xi. 464) has analysed some crystals of durangite, darker in colour than those which he previously examined, with the following results:

As ² O ³	Al ² O ³	Fe ² O ³	Mn ² O ³	Na ² O	Li ² O	F
53.11	17.19	9.23	2.08	13.06	0.65	7.67 = 102.90

The mineral is therefore analogous in composition to amblygonite, which, however, is triclinic, and exhibits totally different optical characters (*2nd Suppl.* 972).

On the mode of occurrence of durangite, see H. Hanks (*Jahrb. f. Min.* 1877, 203; *Chem. Soc. J.* 1877, i. 719).

DURENE, $C^6H^2(CH^3)^4$. This hydrocarbon, originally obtained by the action of sodium and methyl iodide on monobromotrimethylbenzene (bromopseudocumene) (*1st Suppl.* 828), may also be prepared by the action of methyl iodide and sodium on dibromodimethylbenzene (from commercial xylene) diluted with benzene:



The reaction takes place easily at the heat of the water-bath, yielding crystallisable durene, together with liquid trimethylbenzene (*Jahrb. f. Min. 1877, 203; 692; x. 1354*).

DUXITE. A resin occurring in the form of a small layer from 25 to 75 mm. thick, on the lignite of Dux in Bohemia. It is opaque, dark brown, and melts at 246° . Sp. gr. = 1.133. An analysis by Fischer gave, besides 2.72 per cent. water and 1.94 ash—

C	H	S	O
78.25	8.14	0.42	13.19 = 100

(C. Doelter, *Verh. geol. Reichsanst.* 1874, 145).

DYE-STUFFS, or COLOURING MATTERS, ORGANIC (O. N. Witt, *Deut. Chem. Ges. Ber.* ix. 522). All artificial organic dye-stuffs, and likewise those of natural origin—so far, at least, as their constitution is known—appear to belong to the aromatic group, and their tinctorial power may be shown to depend upon certain relations between the radicles of which they are made up. To understand these relations, it is best to consider, in the first instance, the dye-stuffs of simplest constitution, viz. those formed by substitution in a single benzene-molecule.

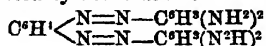
Benzene itself is not a dye-stuff: consequently the tinctorial power of its derivatives must depend upon the substituted radicles or lateral chains; and a comparison of these derivatives will show:—1. That tinctorial power is not possessed by any monoderivative of benzene, or by any di-derivative in which the same radicle is twice repeated; and, in fact, that the only di-derivatives possessing this power are the nitranilines $C^6H^4 \begin{smallmatrix} NO^2 \\ NH^2 \end{smallmatrix}$ and the nitrophenols $C^6H^4 \begin{smallmatrix} NO^2 \\ OH \end{smallmatrix}$, that is to say, those which contain a nitro-group, NO^2 , associated with a salt-forming group, either basylous, (NH^2) , or acid, (OH) . That this association is the essential condition of tinctorial power is shown by the fact that, if the amidogen group be deprived of its basicity by acetylation (substitution of C^2H^3O for H), or the hydroxyl-group of its

acidity by methylation (substitution of CH_3 for H), the tinctorial character is destroyed; the nitro-acetanilides and nitromethyl-phenols, or nitranisols, are in fact colourless bodies.

The body whose presence, in conjunction with a salt-forming group, determines the possession of tinctorial power, may be conveniently called a chromophore, and the compound which requires only the presence of a salt-forming group to convert it into a dye-stuff may be called a chromogen (thus NO_2 is the chromophore of nitraniline and nitrophenol, and nitrobenzene is their chromogen); and the law above mentioned may be stated as follows:

I. The tinctorial power of aromatic bodies is determined by the simultaneous presence of a chromophore and a salt-forming group.

This law holds good likewise in aromatic bodies containing two benzene-rings in their molecules. For example, azobenzene, $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$, which is a compound of deep yellow colour, and benzidine or diamido-diphenyl, $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{NH}_2$, which is a strong base, are not dye-stuffs; but, by uniting the properties of the two, or introducing into the combination both the chromophore, $-\text{N}=\text{N}-$, and the salt-forming group NH_2 , we obtain a series of splendid dye-stuffs such as amidazobenzene, $(\text{C}_6\text{H}_4.\text{NH}_2)_2\text{N}_2$, and oxyazobenzene, $(\text{C}_6\text{H}_4.\text{OH})_2\text{N}_2$. Triamidazobenzene, $\text{C}_6\text{H}_3(\text{NH}_2)_2-\text{N}=\text{N}-\text{C}_6\text{H}_4(\text{NH}_2)$, is the chief constituent of the splendid dye known as Manchester Brown, another constituent of which is a basic substance whose constitution is most probably represented by the formula:



The corresponding oxy-compound, $\text{C}_6\text{H}_4[\text{N}=\text{N}.\text{C}_6\text{H}_3(\text{OH})_2]^2$, which is an acid body, is also a brown of very similar colour.

A further example of the law above stated is afforded by Meyer's azonitromethyl-phenyl, $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{CH}_2(\text{NO}_2)$, which is derived from the acid compound, nitromethane, and is a strong yellow dye, whereas azonitrobenzene, $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4(\text{NO}_2)$, which is neutral, has no tinctorial power.

The colouring matters derived from azobenzene afford evidence of the following law, which is likewise observed, though in a less marked degree, in aromatic bodies containing the benzene-nucleus.

II. The colour-producing influence of a chromophore is exhibited in the saline derivatives of the resulting dye-stuffs, in a higher degree than in those compounds themselves in the free state.

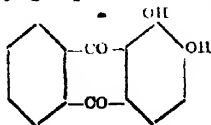
Nitraniline, nitrophenol, and picric acid, in the pure state, are compounds of a somewhat pale yellow colour, but their salts are dark orange-coloured or even red (e.g. those of the chloronitrophenols); again amidazobenzene and oxyazobenzene are yellow, but form saline solutions of a splendid purple or orange colour.

All the dye-stuffs above mentioned contain nitrogenous chromophores; but in the coloured derivatives of anthraquinone the chromophore is a group containing carbon. Anthraquinone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{smallmatrix} \text{C}_6\text{H}_4$, is not a dye-stuff, but alizarin, its dihydroxyl-derivative, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{smallmatrix} \text{C}_6\text{H}_2(\text{OH})_2$, possesses great tinctorial power. Here the group

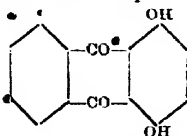
CO , which enters twice, is the chromophore of alizarin, and it performs the same function in the analogous compound diaminanthraquinone, $\text{C}_6\text{H}_4.\text{C}(\text{O})_2.\text{C}_6\text{H}_2(\text{NH}_2)_2$. These bodies lose their tinctorial properties on acetylation, conforming therein to Law I. If, on the other hand, we exalt the salt-forming power of alizarin, as by the introduction of a second OH -group, or of NO_2 or NH_2 , the tinctorial power is likewise increased. Purpurin dyes much more easily than alizarin; so likewise do nitro- and amido-alizarin.

Alizarin also furnishes another illustration of the second law above stated, being of a pale orange colour in the free state or in solution, but forming salts which are dark blue-violet and red in solution, blackish with metallic lustre in the solid state.

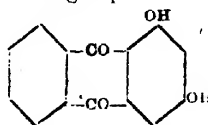
Of the numerous isomerides of alizarin, two only are dye-stuffs, viz. quinizarin and purpuroxanthin (pp. 102, 103); whence it appears that the dioxanthraquinones which are capable of acting as dye-stuffs are those which have at least one of their hydroxyl-groups in the ortho-position with respect to the ketonic groups.



Alizarin.



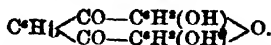
Quinizarin.



Purpuroxanthin.

As a fact having some analogy to this, it may be noticed that *ortho*-toluidine plays an essential part in the formation of rosaniline.

Fluorescein, $C^{12}H^{10}O^2$, and *Eosin*, $C^{12}H^8Br^2O^2K^2$.—The constitutional formula of fluorescein is :



Its chromogen is not actually known, but would doubtless be a colourless body represented by the formula $C^6H^4(CO-C^6H^4)^2O$. Its chromophore, like that of anthraquinone, is double, consisting on the one hand of oxygen, and on the other of the bivalent radicle phthalyl, $C^6H^4(CO)^2$. Phthalyl alone is not a chromophore; phenol-phthalein indeed, though red in alcoholic solution, is not capable of dyeing silk. Fluorescein is a fine yellow dye, but very unstable, being, in fact, of very feeble acid character; but when its acid properties are intensified, as by the introduction of a nitro-group or of halogens, true dye-stuffs are obtained, amongst which the brominated derivatives, viz. the phthaleins and eosin, are especially distinguished by the purity of their colours. This exaltation of the tinctorial power with an increase in the salt-forming properties in the compounds just considered, and, as already observed, in the nitrodiphenylamines and the derivatives of anthraquinone, leads to the following general law :

III. Of two similarly constituted dye-stuffs, that one whose salts are the more stable will have the greater tinctorial power.

Most colouring matters owe their basicity or acidity to the presence of an amido-group or hydroxyl group, whence it follows that each chromogen is capable of yielding two dye-stuffs. Nearly all dye-stuffs may indeed be arranged in pairs, the individuals of which always exhibit the same colour; thus :

Nitrophenol	} pale-yellow	Alizarin	} red or violet.
Nitriline		Diamidanthraquinone	
Pieric acid	} darker yellow	Rosaniline	} red.
Trinitraniline		Rosolic acid	
Amidazobenzene	} yellow	Tetramidotetrazotriphenyl	} brownp.
Oxyazobenzene		Tetrazytetrazotriphenyl	

Dyes produced by the Action of Nitrous acid on the Aromatic Oxy-compounds. Liebermann (*Deut. Chem. Ges. Ber.* vii. 247), by treating phenol with strong sulphuric acid containing nitrous acid, obtained a colouring matter, which was afterwards shown by Baeyer & Caro (*ibid.* 963), to be identical with that which they obtained by the action of sulphuric acid on nitrosophenol (*2nd Suppl.* 911). Baeyer &

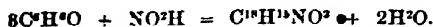
Caro assign to this compound the formula $C^{12}H^{11}NO^2 = N \begin{array}{c} \diagup C^6H^4(OH) \\ \diagdown C^6H^4(OH) \\ OH \end{array}$, Liebermann, on

the other hand, by the analysis of this compound, has obtained numbers leading to the formula $C^{12}H^{11}NO^2$; he has also examined the products obtained in like manner from thymol and from orcin, and finds that the reaction in each case takes place in the same way, 3 mols. of the phenolic compound being always concerned in it. These dyes cannot be obtained in the crystalline state, and therefore, in order to obtain pure products, great care must be taken as to the quantities of the acting substances employed, the temperature of the reaction, &c., and it is best to operate only on small quantities at a time. With some practice it is possible to judge with sufficient accuracy of the purity of the products from the colour of the alkaline solutions. The reagent used for the preparation was in every case a mixture of pure sulphuric acid with 6 per cent. of potassium nitrite.

Dye from Phenol.—To prepare this dye, 5 grams of phenol are mixed with an equal volume of sulphuric acid, the mixture being cooled, to avoid the formation of phenolsulphonic acid; and 20 grams of the reagent above mentioned are then added; the temperature during this operation should be allowed to rise to 40° – 50° , but not higher. The mixture becomes first brown, and then blue at the last stage, and slight evolution of gas takes place. On cooling, the solution is poured into a large quantity of cold water, and the precipitate filtered off and dried.

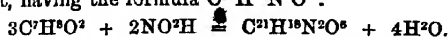
The dye consists of a brown powder, easily soluble in alcohol, and giving with alkalis a deep blue solution.

The analyses of this body agree with the formula $C^{12}H^{11}NO^2$, and not with $C^{12}H^{11}NO^2$, as supposed by Baeyer & Caro. Its formation may be expressed by the equation—

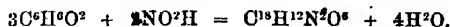


Orcin Dye.—To 10 grams of orcin in 10 grams of sulphuric acid, 40 grams of the reagent are gradually added. The solution should become of a fine purple red.

It is then poured into a large quantity of water, and the orange-red precipitate formed is washed and dissolved in alcohol. After the alcohol has been evaporated off, a green mass is left, having the formula $C^{21}H^{18}N^2O^6$:



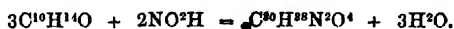
This dye is homologous with Weselsky's diazo-resorcin, which is formed from resorcin thus—



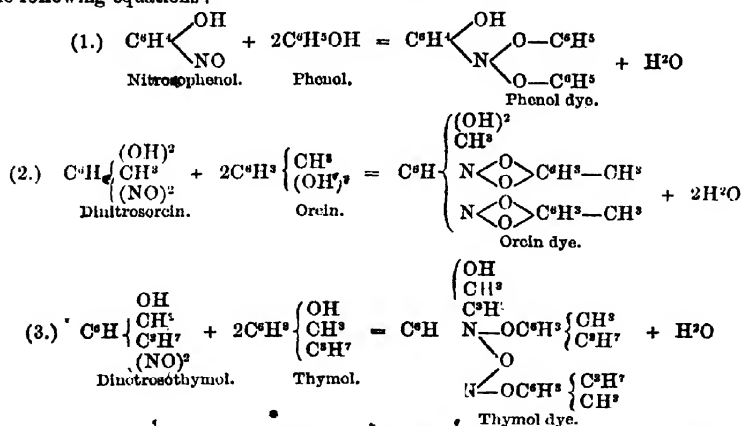
Orcin, treated as above, gives rise in most cases to several colouring matters, which are sparingly soluble in alcohol. The least soluble substance gives with alkalis a bluish-violet solution, with a brown fluorescence, and contains less nitrogen than the preceding body. The orcin dye lately described by Weselsky also possesses a different composition (see ORCIN).

Thymol Dye.—10 grams of finely powdered thymol are mixed with 10 grams of sulphuric acid, and 30 to 40 grams of the reagent added immediately. The solution becomes first green, and then blue. No gas should be evolved. As soon as the reaction is complete, twice the volume of sulphuric acid should be added, to convert unattacked thymol into thymol-sulphonic acid, and after standing for some hours, the solution is poured into water, as before.

The dye consists of a violet-coloured, resinous mass, which gives a violet-red solution with alcohol. Its formula is $C^{30}H^{28}N^2O^4$, and its formation may be expressed thus—



The formation of these bodies probably takes place in the manner represented by the following equations:



Sulphuretted Dyes of Croissant and Bretonnière. These dyes, known in France as 'Grands Teints,' are produced by the action of certain sulphides, or of sulphur and an alkali, at various temperatures, upon almost all organic substances, including all kinds of sawdust, bran, cotton-waste, various organic acids, dragon's blood, gum-resins, &c. They are soluble in water, and adhere to the fibre without a mordant; nevertheless, for reasons to be presently mentioned, they are generally fixed with potassium dichromate. They are cheaper to produce than the aniline colours, in combination with which and with other dyes they yield very beautiful shades of brown, yellow, grey, lilac, and violet, and a colour very nearly approaching to black.

These dye-stuffs are obtained in the shape of bulky, more or less dark-coloured masses, according to the height of the temperature used in their preparation and its longer or shorter duration. Increase of temperature, within the limits of 200° – 300° , and its duration, increase the solubility and the beauty of the product obtained, and its capacity of resisting the action of light. The dyes are all very hygroscopic, and must therefore be preserved in well-closed metal boxes, or they would become oxidised and completely damaged, an insoluble substance being produced; after four or five months' exposure they become quite insoluble and useless. It is important, therefore, to use the dye-bath as fresh as possible and to exhaust its contents before leaving it. In a freshly prepared bath the dissolved colouring matter has such an attraction for

the vegetable and animal fibre that the colour may be entirely withdrawn after sufficient time has elapsed, and a colourless solution left.

In making an aqueous solution of the colouring matter, the water used should be free from lime, which forms flocculent and almost insoluble precipitates with the dissolved colour. Water containing lime should therefore be boiled with soda. The colouring matter is precipitated from its solutions by acids, with liberation of carbonic acid and sulphuretted hydrogen, the precipitate easily re-dissolving, however, in alkaline solutions. Alum and the metallic salts also act as precipitants; but the most important of them for dyeing purposes is potassium bichromate, which also acts as an oxidising agent, and the precipitates which it gives rise to, with few exceptions, are unaffected by most solvents, even boiling caustic lye, so that this salt serves as an important agent for fixing the colour on yarn or cloth. The colours so fixed are also proof against acids, so that ink-spots may be removed from the dyed fabrics by oxalic acid solution of 1 pt. in 4 pts. of water without injury to the colours. Chlorine and hypochlorous acid destroy the colours very quickly. For silk and woollens it is recommended either to partly neutralise the bath with acetic acid, or entirely to precipitate the colouring matter by means of an acid, wash the precipitate, dissolve the latter in ammonia, and dye with the resulting ammoniacal solution (*Chem. News*, xxx. 170; *Dingl. pol. J.* cxxv. 263; *Chem. Soc. Jour.* 1876, i. 458).

On the Dyes produced by the action of Sulphur on Aromatic Diamines, see PHENYLENE-DIAMINES.

Decoloration of Indigo-solution and other Vegetable Dyes by various Sulphur-compounds.—The bleaching of indigo-solution, by sulphur-compounds, more particularly hyposulphurous acid, H_2SO_3 , and the hydrogen persulphides (H_2S^2 and H_2S^3), is generally attributed to the reduction of indigo-blue to indigo-white, a view which derives support from the circumstances that when the bleached solution is shaken with air the blue colour is restored. According to E. Schaer, however (*Deut. Chem. Ges. Ber.* ix. 340), the bleaching is more probably due to the formation of molecular combinations of the sulphur-compounds with indigo, whereby the colour of the latter is masked. For a solution of indigo bleached by hyposulphurous acid is turned blue not only by atmospheric oxygen and all oxidising agents, but also by several reducing agents, especially hydrogen sulphide; and a solution bleached by hydrogen persulphide is turned blue by treatment with gaseous sulphur dioxide or its aqueous solution, as well as by oxidising substances;—facts which admit of easy explanation on the supposition that hydrogen sulphide in this case acts upon hyposulphurous acid in the same way as upon sulphurous acid, and that hydrogen persulphide behaves like hydrogen sulphide towards sulphur dioxide.

According to this explanation, indigo and other vegetable dyes bleached by hyposulphurous acid or hydrogen persulphide would be restored to their original colours by treatment with any substance which decomposes these sulphur-compounds, and thus sets free the colouring matters.

Testing of Dye-stuffs. The following systematic method is given by F. Fol (*Dingl. pol. J.* cxxii. 520):

BLUES.—Solution of citric acid or dilute hydrochloric acid is added.

(a.) Colour changes to red or orange: *Logwood blue*.

(b.) Colour does not change.

Another part is treated with calcium chloride solution.

(a.) Colour remains unchanged: *Prussian blue*.

(b.) Colour changes.

Another part is treated with caustic soda.

(a.) The substance is decolorized: *Aniline blue*.

(b.) It remains unchanged: *Indigo blue*.

YELLOWS.—A portion is tested for ferric oxide by means of potassium ferrocyanide; another part is tested for picric acid by means of potassium cyanide solution. The production of a blood-red colour indicates picric acid.

If the colours do not appear, another portion is treated with a boiling soap-solution (1 part of soap in 200 of water).

(a.) The colour changes to brown, but becomes yellow again with an acid: *Turmeric*.

(b.) The colour becomes very dark: *Fustic*.

(c.) The colour remains unchanged: *Weld*, *Persian berries* or *Quercitrus*.

Another portion is boiled with stannous chloride.

(a.) The colour remains unchanged: *Quercitrus*.

(b.) The colour changes to orange: *Persian berries*.

If *annatto* is the colouring matter present, the colour changes to greenish blue on boiling in concentrated sulphuric acid.

REDS.—The substance is treated with boiling soap-solution.

- (a.) The colour is totally discharged: *Saffron carmine*.
- (b.) The colour is slightly discharged: *Aniline red*.
- (c.) The colour changes to yellowish-red or yellow: *Brazil wood* or *Cochineal*.
A part of the substance is treated with concentrated sulphuric acid.
 - (1.) A cherry-red colour is produced: *Brazil wood*.
 - (2.) A yellowish orange colour is produced: *Cochineal*.
- (d.) The colour remains unchanged: *Madder red*. This colour is not discharged by ammonium chloride, or by a mixture of equal parts of stannous chloride, hydrochloric acid, and water.

GREENS.—These colours may consist of a mixture of blues and yellows, or of such substances as aniline green.

The substance is heated in a water-bath with alcohol of 95 per cent.

(I.) The alcohol is coloured yellow, while the substance becomes more and more blue: *Indigo* or *Prussian blue* is present. The residue is washed and tested for these blues, as already directed. The alcoholic liquid is tested for yellows, as above.

(II.) The alcohol is coloured green, while the substance becomes less coloured: *Aniline green* or a mixture of *Aniline blue* with yellow is present.

A part of the substance is boiled with dilute hydrochloric acid.

- (a.) The liquid is coloured blue or lilac: *Aniline green* from *methyl iodide* is present.
- (b.) The substance is decolorised: *Aniline green* from *aldehyde*.
- (c.) The substance is coloured blue, while the liquid becomes yellow: *Aniline blue* mixed with yellow.

VIOLETS.—The substance is boiled in calcium chloride solution.

- (a.) It is unchanged: *Alcanna violet*.
- (b.) It is coloured nanguen yellow: *Madder violet*.
- (c.) It is decolorised: *Cochineal violet*.

Another portion is boiled in citric acid; the colour is lightened: *Aniline violet*.

To distinguish between the two aniline violets, a third part is boiled in hydrochloric acid, which is diluted with three times its volume of water. After washing it appears blue-violet if ordinary aniline violet is the colour, while if Hofmann's violet is present, the substance appears greenish, and after washing light lilac or bluish.

On the behaviour of dye-stuffs with various reagents, see also Bibarow (*Moniteur scientifique* [3], iv. 500; *Chem. Centr.* 1874, 700, 717).

Use of Sodium Hyposulphite, Na₂SO₃, in examining the Colouring-matters of Dyed Fabrics.—Cloth dyed with litmus is bleached instantaneously by this reagent, even in the cold; cloth dyed with Brazil-wood is bleached after a very short time. A cloth which had been dyed with indigo over another colour, was found, after digestion for some time with hyposulphite, to exhibit the under colour only. The reaction is facilitated by rendering the liquor alkaline with potash or soda and by heating, but not to boiling. The rapid oxidation of the hyposulphite renders it of but little value in determining the amount of litmus in the commercial substance or in tinctures (Scurati-Manzoni, *Gazz. chim. ital.* vi. 318).

Testing of the Fastness of Dyes on Coloured Fabrics.—Red dyes should not colour soap-water or lime-water when boiled therewith, and the fabrics themselves should not be altered in colour by this treatment. The occurrence of these negative results shows the absence of Brazil-wood, archil, safflower, sandal-wood, and tar-colours. The only fast yellow dye is madder yellow. On boiling stuffs dyed with it with water, alcohol, and lime-water in succession, no colouring is withdrawn from the material and the liquid remains colourless. Fast blue dyes should not give up any colouring matter when boiled with alcohol or warmed with a mixture of hydrochloric acid and water or alcohol. Violet dyes are unstable if they give up their colour in any considerable degree when boiled with weak spirit (equal parts of water and ordinary spirit of wine), and left to stand for ten to fifteen minutes, or if, on boiling with dilute hydrochloric acid, they change in colour to brown or brown-red, and impart a red colour to the liquid. Orange dyes should not be dissolved out by boiling water or warm alcohol. Green dyes boiled with alcohol should not colour it either blue, green, or yellow; and hydrochloric acid heated with green-dyed stuffs should not acquire either a red or a blue colour. Brown dyes are unstable when they give up red colour on boiling with water, or yellow on being left in contact with alcohol. If a black stuff, when boiled with hydrochloric acid and water, colours the liquid only yellow, the black is fast (tannin-black). If the colour of a fresh sample changes to brown on boiling with sodium carbonate, nothing but tannin-black is present; but if the stuff thus treated remains black or turns blue, there is a basis of indigo under the

true tannin-black. If the black stuff, on being boiled with water and hydrochloric acid, colours the liquid red, and is itself at the same time turned brown, the dye is logwood, without a basis of indigo, and is quite unstable: if, however, the stuff when thus treated turns blue and the liquid red, there is a basis of indigo under the logwood, and the dye has a certain degree of stability (W. Stein, *Dingl. pol. J.* cxx. 216).

Use of Epsom Salts and Sulphurous Acid in Dyeing. It has been long remarked that woollen goods dyed with aniline colours, and treated with Epsom salts, stand the action of soap and soda, and the dressing process generally, better than those which have not been so treated, or treated with any other substance. Reimann advises the use of Epsom salt in yarns to be dyed violet. The magnesium salt is then decomposed by the action of soda, with separation of insoluble magnesium compounds, which exert no action upon the colouring matter; any alteration in the colour by the alkali is thus prevented.

All woollen-dyers are agreed that in dyeing with methyl- and dahlia-violet, the use of sulphurous acid is found very advantageous; the brightness and clearness of the tint being thereby considerably increased (*Dingl. pol. J.* cxx. 316).

On the Dyeing of Straw, Hair, Felt, and Feathers, see *Dingl. pol. J.* ccviii. 156, 239, 318; *Jahresb. f. Chem.* 1872, 1074; 1873, 1127; of Caoutchouc, *Dingl. pol. J.* cxx. 315; *Jahresb.* 1873, 1127. On the production of Brocade colours on carpets, gypsum, glass, &c., see *Dingl. pol. J.* ccvii. 269; ccviii. 159; *Jahresb.* 1873, 1126.

The following methods of analysing dynamite are given by Champion a. Pellet (*Moniteur Scientifique* [3], iii. 1036). 1. If the dynamite consists of a mixture of nitroglycerin with silica or other inert materials, 30 grms. of it are treated with ether, and the extract is evaporated at a gentle heat on a water-bath till the weight of the residual nitroglycerin becomes constant. 2. Dynamites with active base usually consist of mixtures of nitroglycerin with sodium nitrate, coal-dust, resin, and ferric oxide, which decompose during the explosion, yielding gaseous products which increase the explosive power. These are first treated with ether, which dissolves the resin and the nitroglycerin; the ethereal solution is then evaporated; the residue weighed and redissolved in ether; and then the liquid is poured into a boiling solution of sodium carbonate, which dissolves the resin and precipitates the nitroglycerin. The resin is precipitated from the alkaline solution by hydrochloric acid, then collected on dried and weighed filters, and weighed. In the residue left after exhaustion of the dynamite with ether, the sodium nitrate is determined by extraction with water, and the carbonaceous matter and ferric oxide by ignition.

Another method, given by the same authors (*Bull. Soc. Chim.* [2], xix. 496), for the estimation of nitroglycerin in dynamite, is to exhaust the substance with wood-spirit, and evaporate to a constant weight. If the dynamite contains resin, saltpetre, &c., it is treated with hot water, whereby the nitrates are dissolved, and the resins separated on the surface of the water. The nitroglycerin is then separated from the insoluble matters with wood-spirit as above.

On the Conditions of Explosion of Dynamite, see EXPLOSIVES.

A description of the arrangements and mode of working in Nobel's Dynamite factory at Lauenburg is given in the *Berichte der deutschen Chemischen Gesellschaft*, 1876, 1800; shortly also in the *Jahresb. f. Chemie*, 1876, 1107.

DYSIOTE. An alloy of copper, 62.30 per cent., lead, 17.75, tin, 10.42, and zinc, 9.20, with traces of iron, used in Germany for the axle-beds of machinery. It may be prepared by fusing together 62 pts. copper, 18 lead, 10 tin, and 10 zinc. It is not quite homogeneous (Uhlenhuth, *Dingl. pol. J.* cxcv. 377).

DYSODIL. This carbonaceous mineral, originally found at Melilli in Sicily (ii. 360), occurs also in the Ries district of Bavaria, where also brown coal is found in strata, at a depth of 8 to 9 meters, in a bluish-grey loam. Dysodil occurs at the same depth as the brown coal, but only in thin strata or layers, in the form of black parchment-like leaves, which become brown on being dried. These leaves are united together by interpolated loam, which thus causes the layers to have a thickness of several centimeters. From these layers extremely thin leaves of dysodil can be separated by means of a knife, but it is impossible to free them entirely from adhering loam: for, if the dry mineral is scraped with a knife, dysodil and clay come off together, and if washing the substance is attempted, the loam behaves like fuller's earth. Sp. gr. about 1.458. Examined under the microscope, it exhibits a uniform, finely undulating, gritty structure, in which few crystals are discovered. The homogeneous ground-mass in which they are found seldom exhibits any signs of organic structure. The crystals are tabular, not attacked by acetic or hydrochloric acid, but are rounded

off by ether. The action of ether never goes beyond this point, even if the dysodil has been exposed to it for several days, and only partial solution occurs.

Dysodil is characterised by burning easily with a brightly luminous flame, giving off a disagreeable odour much like that of burning caoutchouc. If cut into thin strips and freed from clay it burns like a wax taper, with a very sooty flame. On submitting the air-dried dysodil to destructive distillation, water comes over at 50° , and is eventually completely driven out. At 170° and above it evolves a large amount of illuminating gas, which contains 2 per cent. of carbonic acid and a trace of sulphuretted hydrogen. The smell of this gas and also that of the tar coming over at 220° – 260° recalls that of allyl. The tar runs out in deep yellow drops. The reaction of the products of distillation of the gas-water and of the oil is decidedly alkaline, whence it differs from the products of the destructive distillation of brown coal, which are acid. Dysodil coke still retains the parchment-like appearance of the original substance; it is black, and gives off a further amount of illuminating gas when ignited in a platinum crucible, leaving eventually a reddish-grey ash. 100 parts of crude dysodil dried at 100° consist of:—

Ash*	C	H	N	S	O	H ² O
69.464	10.353	3.82	0.189	0.601	5.843	0.73 =, 100.

Deducting the ash, we get the true composition of dysodil, namely:

C	H	N	S	O	H ² O
63.39	12.61	0.62	1.96	19.13	2.39 = 100.00

(Fricklinger, *Jahrb. f. Min.* 1875, 760). See also Church (*Chem. News*, xxxiv. 155).

E

EARTH-METALS. From a comparison of the composition of the selenites of glucinum, cerium, didymium, lanthanum, yttrium, erbium, and thorium with that of the selenites of well-known metals such as magnesium, nickel, cobalt, copper, zinc, manganese, aluminium, iron, and chromium, E. Nilson (*Deut. Chem. Ges. Ber.* viii. 656) infers that glucinum is analogous to the metals of the magnesium group, that is to say, it is bivalent; that erbium, yttrium, and the cerite metals are analogous to aluminium, i.e. trivalent, whilst thorium occupies a place by itself, having no apparent relation either to the other metals of the rarer earths or to tin or zirconium. See further Nilson (*Ber.* ix. 1142; *Chem. Soc. Jour.* 1877, i. 49; also CERITE METALS (p. 418), and ERBIUM (p. 736 of this volume).

On the Compounds of the Chlorides of the Earth-metals with Mercuric Cyanide, see CYANIDES (p. 610).—On Other Compounds of the Earth-metals, see SELENITES, CERITE METALS (pp. 418–425), and ERBIUM in this volume.

See RESINS, FOSSIL.

Reaction with Cellulose.—According to A. Müller (*J. pr. Chem.* lxxxiii. 384), baryta is precipitated from its aqueous solution in somewhat considerable quantity by filter-paper; and H. Weiske finds that strontia and lime are precipitated by filter-paper in the same manner: hence in quantitative determinations the alkaline solutions of these bodies should not be filtered (*Landn. Versuchs.-Stationen*, xix. 155).

EARTHS, EATABLE. Earth-eating is known to be practised by various races of people in different countries. In Spain, there is the *bucaro*; in Thuringia, the *beurre de roche*; in Russia, the *farine de roche*, or *farine céleste*; in Hindostan, the so-called *pūtina-earth*; on the island of Java, a species of earth called *teneampa*, and others, all of which are made use of by the inhabitants as food. At the general meeting of the Hungarian Pharmaceutical Society, in 1875, a note was read by J. Molvar, on a species of earth used as food by the poorer classes of the Ne district in Hungary in times of famine. The following results show the analy-

* CaCO_3 , Al_2O_3 and SiO_2 .

this earth:—Carbonic acid, 40·357; lime, 51·488; magnesia, 0·11; volatile matter, 5·545; ferrous oxide, 0·168; alumina, 2·272. The volatile matter, which is the probable source of nourishment, was found to contain, besides empyreumatic substances, 0·067 water, and 0·010 nitrogen. J. Brix (*Chem. Centr.* 1875, 542).

C. Schmidt (*Ann. Ch. Phys.* [4], xxvi. 535) has examined two edible earths, one from Lapland, the other from Southern Persia.

The Lapland earth came from the village of Ponoï, 67° 5' N., 42° 12' E. It is a light white powder, resembling talc, used in Lapland for mixing with dough for bread. A bed of it 2 or 3 feet thick, exists under the sand and clay of the river Atache Rjeka. It consists essentially of finely divided potassium silicate, appearing, when magnified 200–300 times, in white non-crystalline scales, but little attacked by hydrochloric or sulphuric acid. It contains in 100 parts, alumina, 40·797; potassium, 45·506; silica, 9·845; water driven off at 100°, 0·260; water removed at a low red heat, 0·835. It is probable that this so-called edible earth plays only a passive part in alimentation.

The second specimen of earth, from Kirman, in Southern Persia, is known under the name of *G'hel i G'ueh*, and occurs in white and grey lumps, soluble with strong effervescence in dilute nitric and hydrochloric and in warm acetic acid, leaving a slight residue of silica. It contains in 100 parts, CO_2 45·723, MgO 32·722, CaO 13·235, NaCl 3·542, water at 120° 1·558, hygroscopic moisture, 1·422. Schmidt regards this earth as a purely mechanical mixture of magnesium and calcium carbonates, with a little magnesium hydrate, acting on the system in the same way as *magnesia alba*. It is in great part soluble in carbonic acid water.

EBULLIOSCOPE. A description of Vidal's Ebullioscope for determining the strength of spirituous liquors by their boiling points is given in the *Compt. rend.* lxxviii. 1470, and in the *Journal of the Chemical Society*, 1874, 1014.

ECBOLINE. See ERGOT.

ECHICACOUTCHIN, ECHICERIC ACID, and ECHICERIN. Constituents of Dita bark (*Echites scholaris*). See p. 689.

• **ECHINODERMATA and TUNICATA.** The mineral constituents of these animals have been examined by A. Hilger (*Pflüger's Archiv. f. Phys.* x. 212). The bodies of the *tunicata* (ascidians, &c.), exhausted with dilute hydrochloric acid, and not incinerated, were found to yield traces of sodium chloride, small quantities of silicic acid, calcium sulphate, and phosphate, and traces of iron, whilst carbonates of the alkaline earths were absent.

The skeleton or covering of the Echinodermata (Holothuria) was found to yield, when treated with dilute hydrochloric acid, the following substances: sodium chloride and sulphate, calcium sulphate in abundance, calcium carbonate and phosphate, silicic acid, magnesium carbonate, and ferric oxide.

The abundance of sulphate probably plays an important part in ministering to the growth of chondrogenous substance.

ECHIRETIN, ECHITEIN, and ECHITIN. See DITA BARK.

ECLOGITE. This rock, occurring at Eibiswald, in Styria, has been examined by J. Mauthner (*Jahrb. f. Min.* 1873, 323). It consists of a granular mixture of garnet, omphacite, hornblende, and a small quantity of quartz. The garnet encloses minerals of various kinds which are grouped round the centre of the crystals. The following analysis (the first that has been made of an eclogite) is by E. Ludwig:—

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
50·13	14·37	13·02	6·46	12·85	2·35	0·14
= 99·82.						

Three varieties of eclogite from Upper Franconia have been analysed by E. v. Senebster (*Liebig's Annalen*, clxxi. 183).

I. From Eppenreuth, near Hof; containing large garnets of reddish-brown colour, beautifully crystallised; also grass-green granules of omphacite, small radiated crystals of diathene, and colourless quartz. Powder white, or faintly red. Sp. gr. 3·40.

II. From Silberbach, near Conradsreuth. It had a fibrous, radiated appearance, due to the predominance of leek-green omphacite, and contained very large garnets, but less diathene and quartz than the preceding specimen. Powder grey. Sp. gr. 3·42.

III. From Markt Schorgast; containing a large number of garnets, and exhibiting black-brown veins of carinthine between large, pale-green crystals of smaragdite, with a little omphacite and diathene. Powder greyish-green. Sp. gr. 3·43.

Analyses of Eclogite.

	I	II	III
Silica	57.10	55.00	48.81
Phosphoric anhydride	traces	traces	traces
Alumina	11.66	13.54	16.25
Ferric oxide	2.84	2.74	6.00
Ferrous oxide	3.22	3.37	7.48
Manganous oxide	0.31	0.20	0.43
Lime	13.80	12.09	9.72
Maghesia	6.37	10.21	7.52
Potash	0.81	0.50	0.46
Soda	2.21	2.10	2.64
Water	0.54	0.32	0.12
	98.86	100.07	99.43

The proportion of the garnets to the general substance or 'ground-mass' of the rock is 1 : 3 in the eclogites from Eppenreuth and Silberbach, and 1 : 1 in that from Markt Schorgast. The first two, which contain typical omphacite, have approximately the following mineralogical composition: 25 per cent. garnet, 4.5 quartz, disthene, and mica, and 70.5 omphacite, whereas in the third, which contains hornblende, the proportion of garnet rises to 60 per cent.

On the Eclogite of the Saxon Granulite district, see Dathe (*Jahrb. f. Min.* 1876, 225, 337; *Chem Soc. J.* 1876, ii. 387, 612).

EGGS. The presence of starch in egg-yolk has been demonstrated by Dareste (*Vierteljahrsschrift f. prakt. Pharm.* xxii. 265). The reaction of the starch with iodine is in general much hindered by the presence of the fatty and albuminous constituents of the egg, so that it is best to undertake the microscopical examination when the yolk-sac has been separated from its contents by the process of hatching. At this stage distinct starch granules may be recognised, not exceeding 0.025 mm. in diameter, and frequently turned red instead of blue by iodine. Dareste believes that he has seen three or four generations of starch-granules, which are formed from glucose and reconverted into it. Starch-granules of 0.005 mm. diameter occur also in the seminal ducts of birds, and other animals (not specified), at times different from the breeding season, at which indeed they disappear wholly or partially.

Crystals in Eggs.—Some eggs, which were no longer fresh, but yet had not undergone the ordinary putrefactive process, were found to be free from microscopic organisms, but to contain groups of minute acicular crystals attached to the membrane which lines the shell. These crystals proved to be tyrosine, and the contents of the eggs also yielded leucine. These substances were obtained in much larger quantities from the merely stale eggs above mentioned than from putrid eggs, and there seems, therefore, to have been a transformation of the albumin resembling that which Schützenberger observed in the insoluble proteic components of beer-yeast, when that plant continues to live at its own expense without putrefaction (*U. Gayon, J. Pharm. Chim.* [4], xxii. 27).

Spontaneous Alteration of Eggs.—Gayon finds that spontaneous decomposition occurring in eggs is invariably accompanied by the presence of microscopic organisms (vibrios), which he supposes to be introduced through the oviduct during the formation of the egg. It has been stated by previous observers that when eggs are shaken so as to mix the yellow and white, immediate putrefaction occurs. This, however, according to Gayon, is far from general. An intimate mixture of the yolk and white of egg, passed into vessels deprived of germs, may be kept for months exposed to pure air at a temperature varying from 20° to 30° without undergoing putrefaction; but if the experiment be tried with an egg containing bacteria or spores of fungi, and these pass over into the mixture, putrefaction in the case of the former, and change due to the growth of fungi in the case of the latter, will occur. In these experiments, as in those of Pasteur, all conditions favourable to spontaneous generation are present, but still it does not occur. The molecular granules which are present, especially in the yolk, do not give rise to bacteria. Hence Gayon concludes, in opposition to Béchamp, that the granules which the latter calls *microzymes*, have not the power of converting themselves into bacteria or vibrios, any more than into globules of alcoholic yeast.

The following experiment points to the same results. If during the incubation of an egg the development of the embryo be arrested at any period before the exit of the chick, and if such eggs containing dead embryos be kept for several months at about 25°, some only of them will be found putrefied, whilst the others will have undergone a slow non-putrefactive process. Contrary to the hitherto published observations, Gayon finds that the putrefaction of the embryos of eggs is always accompanied by the

development of bacteria or vibrios analogous to those found in the putrefaction of ordinary eggs. He confirms the views of previous observers that fungi may develop in the interior of eggs and produce special changes. Bacteria and fungi may co-exist, the egg being both putrid and mouldy, but in this case the putrefaction is due to bacteria and not to fungi.

Another change, acid fermentation, has been met with in a few cases. In these the eggs exhale an acid non-putrid odour, and contain, not bacteria, but spicules varying in breadth from $\cdot 5$ to $\cdot 7$, and in length from δ to 10-thousandths of a millimeter.

Lastly, eggs, like all organic matter, may undergo slow oxidation, which does not correspond with the development of any microscopic organisms. This is characterised by a yellow tint and the presence of numerous very fine crystalline needles (*Compt. rend.* lxxvi. 232; lxxvii. 214).

On the Decomposition of Eggs, see also W. Thomson (*Chem. News*, xxx. 159; *Chem. Soc. J.* 1875, 175).

Preservation of Eggs.—According to F. C. Calvert (*Compt. rend.* lxxvii. 1024), eggs, either entire or pierced at the end by a fine needle, may be kept for three months without change in an atmosphere of nitrogen, hydrogen, or carbonic anhydride. In dry oxygen entire eggs undergo no change, but if the gas is moist, the egg becomes covered with a white filamentous mould.

An egg pierced at the end soon becomes putrid, either in dry or in moist oxygen, the amount of oxygen consumed, and of carbonic anhydride and nitrogen evolved, being much greater in the latter case than in the former. See also H. Vohl (*Deut. Chem. Ges. Ber.* ix. 22; *Jahresb. f. Chem.* 1876, 1133).

Eggs of Reptiles.—The yolk of the egg of the common snake contains a proteid resembling myosin, lecithin and its products of decomposition, also cholesterol, alkali-albuminate, fat (8.9 p.c.), phosphates, chlorides and sulphates of the alkalis. The shell contains carbonate and phosphates of calcium, traces of silica and iron, but no manganese; calcium sulphate is present, and indeed appears to be a general constituent of the body of the lower animals, as it exists in the outer integument of *Holothuria*, *Tunicata* (*Pyrosoma ind.*), *Salpæ*, *Phallusia*, &c.

The shell and yolk also contain an organic substance consisting of C. 54.68, H. 7.24, N. 16.37, and O. 21.10. This body is free from sulphur and phosphorus, and forms in the dry state a yellowish, horny mass, insoluble in alcohol, ether, acetic acid, and dilute hydrochloric acid; with water it softens and swells up. The composition is similar to that of elastin, from which it differs, however, by not being acted upon by concentrated caustic potash (Hilger, *Deut. Chem. Ges. Ber.* vi. 165).

§ (ii. 366). The following three analyses (A–C) of eh-lite from Cornwall have been published by Church (*Chem. Soc. J.* 1873, 118). D is the percentage composition calculated from the formula $5\text{CaO} \cdot 12\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$:

	CaO	P ₂ O ₅	As ₂ O ₃	Fe ₂ O ₃	H ₂ O	Sp. gr.
A (found)	66.29	20.38	2.42	1.42	8.25 = 98.76	3.911
B "	66.84	23.73	trace	—	9.26 = 99.83	3.911
C "	66.88	23.96	trace	—	9.16 = 100	4.23
D (calc.)	66.98	23.92	—	—	9.10 = 100	—

* By difference.

A specimen of the fibrous variety of scapolite, so named, from Arsdale's Quarry, Bucks Co. Pennsylvania, was found by Leeds (*Sill. Am. J.* [3], vi. 20) to contain:

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O
47.47	27.51	trace	1.20	17.59	3.05	1.40	1.48 = 99.70.

Sp. gr. = 2.708 (compare v. 203).

ELÆOCOCCA. (Cloeæ, *Compt. rend.* lxxxi. 469; lxxxii. 501; lxxxiii. 943). *Elæococca vernicia*, Tong-Yeu, or the oil-tree of China, is a plant of the Euphorbiaceous order. Its fruit is a capsule containing several large, tough-coated seeds, which yield by cold pressure about 35 per cent. of their weight of a rather viscid, colourless, inodorous oil, having a specific gravity of 0.9362 at 15°, and thickening but not crystallising at -18° . Ether extracts about 41 per cent. of the same oil. If, however, carbon sulphide be used as the solvent, the extracted fatty matter solidifies on cooling to a mass having a crystalline structure, melting at 34° , and having the same composition as the liquid oil: the action of the carbon sulphide has therefore given rise to a physical modification of the fatty matter. The oil likewise solidifies when heated in contact with the air, but in this case the solidification is attended with absorption of oxygen, and the product is nearly insoluble in ether and in carbon

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sulphide, and does not melt at 200°. Lastly, solidification is effected by exposing the oil to light, even without contact of air, two days of insolation sufficing for the purpose.* The solidification is due to the action of the more refrangible rays, as it does not take place under yellow glass. The solid fat produced has the same weight as the original oil, melts at a temperature 32° higher, is perfectly neutral to test paper, does not contain any free fat acid, and does not yield glycerin to water.

* Oil of *elaecocca* dries up in a few hours, when spread in a thin film on a plate of glass and exposed to the air; it is, in fact, one of the fastest-drying of all known oils. It is easily saponified by alkalis. When heated in a close vessel with alcoholic potash, it is resolved into glycerin and a soap, which when decomposed by phosphoric acid yields two acids, one liquid, which is ordinary *oleic acid*,* and yields a lead salt soluble in ether; while the other, called *elaemargaric* or *margarolic acid*, is crystalline, and yields a lead salt insoluble in ether. The oil is therefore a mixture of two glycerides, viz. *elaemargarin* (about 75 per cent.) and ordinary *olein*.

Elæomargaric acid, $C^{17}H^{30}O^2$, crystallises in rhomboidal plates; it melts at 48°, is insoluble in water, soluble in ether, carbon disulphide, liquid hydrocarbons, and aqueous alcohol; it rapidly absorbs oxygen, and is converted into a soft transparent body, which gradually becomes hard and resinous. The acid gains 8.5 per cent. in weight on exposure to air for a fortnight, but may be kept without alteration in a sealed tube or under water. It is monobasic. The *potassium salt*, $C^{17}H^{30}O^2K$, crystallises easily from hot alcohol. Its concentrated aqueous solution is decomposed by dilution, yielding an acid salt which crystallises in nacreous scales. The *lead salt* is insoluble in ether.

The solid fat obtained by insolation of the oil yields by saponification a mixture of solid fatty acids, but no liquid acid. By a series of crystallisations from alcohol, a solid acid may be separated, called by Cloez *elæostearic acid*, which melts at 72°, may be distilled under reduced pressure, and is probably a polymeride of *elæomargaric acid*.

ELAÏDIC ACID. See OLEIC ACID.

According to J. Lehmann (*Dingl. pol. J.* cexix. 94), the press cakes of the seeds of *Elais guineensis*, the so-called palm-cakes, contain:

Fat	7.12 to 15.14 per cent.
Proteids	12.85 to 20.25
Non-azotised extractive matters	22.61 to 50.58
Woody fibre	12.86 to 28.50
Ash	2.79 to 4.41
Water	9.61 to 12.35

ELASTICITY. II. Buff (*Pogg. Ann. Jubel.* 349) has determined the coefficients of elasticity of metals and other solid bodies by means of flexure experiments made with rods supported at both ends and loaded in the middle. The results are contained in the following table:

	Coefficient of Elasticity		Coefficient of Elasticity
Cast steel	20960	Copper	12270
"	21056	Zinc	11900
Bar iron	19760	"	10800
"	19790	Lead	1862
"	20940	White glass	7490
"	20860	Oak-wood	835
"	20900	Deal	1699
Cast iron	14352	Beech-wood	959

On the Elasticity of Tension of Metals at various temperatures, see Pisati (*Gazz. chim. ital.* vi. 23; *Chem. Soc. J.* 1877, i. 38). On the Elasticity of Gases, see GASES. On the Elasticity of Torsion: Pisati (*Gazz.* vi. 57; vii. 61, 173; *Chem. Soc. J.* 1877, ii. 162, 700).

Elasticity of Regular Crystals in different directions.—The experiments of Voigt on the tenacity of monometric or regular crystals in different directions gave, for the relation between the minimum and maximum elasticity, the ratio 1 : 1.22. P. Groth, proceeding on the principle that the rate of transmission of sound in solid bodies is dependent on their elasticity, has determined the minimum and maximum elasticity of rock-salt by means of the nodal lines produced upon a vibrating rod of that substance 80 mm. long and 2 mm. thick, and has found it to be as 1 : 1.19, a result which may be regarded as identical with that of Voigt. These results show that the molecular condition of monometric crystals is different from that of amorphous bodies (*Jahrb. f. Min.* 1876, 199).

* Originally regarded by Cloez as a peculiar acid, and designated as *eleoleic acid*.

(*Sambucus nigra*). The ash of the bark of this tree contains

in 100 parts:—

K ² O	Na ² O	CaO	MgO	Al ² O ³	Fe ² O ³	Cl	SO ²	P ² O ⁵	SiO ²	CO ²
13.956	0.965	30.924	10.730	0.250	0.350	0.179	5.818	8.045	5.455	23.274

(Wittstein, *Arch. Pharm.* [3], vii. 394).

ELECTRICITY. VOLTAIC CIRCUITS.—Experiments bearing on the theory of voltaic action have been made by Gladstone and Tribe (*Proc. Roy. Soc.* xxiv. 47). They find that a zinc-platinum couple, immersed in a solution of potassium chloride, liberates potassium against the platinum plate, as evidenced by the evolution of hydrogen and the presence of free alkali, and that a similar result is obtained with the chlorides of ammonium, sodium, barium, strontium, and magnesium. The action is slow, but becomes quicker when magnesium is substituted for zinc in the couple. Now according to the chemical theory, the zinc-platinum couple can act only when the electrolytic liquid in the cell contains an element (generally hydrogen), which is less positive, or has less affinity for Cl, SO², &c., than zinc; but in the experiments above described the zinc appears to be capable of replacing metals more positive than itself: hence it would appear that the ordinary chemical theory of the battery requires some modification.*

Sulphates and nitrates are also decomposed in the same manner as chlorides, and a metal joined to another more electronegative than itself is capable of decomposing its own salts: thus a mercury-gold couple will decompose mercuric chloride, mercury being deposited upon the gold.

With the view of throwing light on the contact theory of voltaic action, J. E. Fleming (*N. Arch. Ph.* nat. l. 412) has constructed a battery without contact of dissimilar metals. This battery, which has an electromotive force of $\frac{1}{2}$ -Daniell, consists of a series of cells containing alternately dilute sulphuric acid and an alkaline solution of sodium pentasulphide, and connected by U-shaped strips of copper and lead alternately. The number of the cells is even, so that the first and last contain different liquids but the same metal, lead for example; and these can be connected with a galvanometer by two strips of copper immersed in them. In the nitric acid cells the copper being the more strongly attacked is positive towards the lead; but in the sodium sulphide it is negative: consequently all the cells produce a current in the same direction.

Currents produced by the Successive Immersion of Electrodes in different Liquids.—When two electrodes of mercury (or other metal) connected by a galvanometer wire, are successively immersed in a conducting liquid which does not act upon them, such as water, alcohol, glycerin, saline solutions, hydrochloric acid, &c., an electric current passes from the freshly wetted surface of the mercury to that which had been wetted first. The strength of this electric current diminishes with the increasing resistance of the intervening liquid, and its electromotive force varies with the nature and the concentration of the different liquids, but decreases as the saline solution becomes more concentrated; it may amount to 0.6 of the electromotive force of a Daniell's cell. The electromotive force is the greater, the more quickly the surface of contact between metal and liquid, at the last immersed electrode is formed; and as the rapidity with which this takes place is increased, the electromotive force approaches a maximum which, in the case of viscous liquids, such as glycerin, is very soon attained, and is totally independent of the capillary constant at this surface of contact. These electric currents are probably caused by changes in the molecular condition (different density or concentration), which is gradually brought about near the surface of contact of the two liquids.

The electric currents produced by successive immersion of two mercury electrodes in sulphuric or nitric acid, owe their origin chiefly to the substances formed by the chemical action of the acid upon the mercury, and must therefore be considered as secondary phenomena or as polarisation currents. Electrolysis is capable of changing the surface-tension at the common boundary between mercury and other conducting liquids, the change consisting either in an increase or a decrease, and altering its sign with the direction or duration of the current. The disturbances brought about by capillary phenomena cannot be ascribed to the substances which have been separated by electrolysis (Quincke, *Pogg. Ann.* cliii. 161).

Function of Peroxides in the Voltaic Circuit.—In a battery arranged on Leclanché's principle (1st Suppl. 555) the carbon cylinder being surrounded with a mixture of fine or coarse carbon powder and fine or coarse manganese dioxide, it was found by comparative experiments that the strongest and most constant currents were produced

* Does not the aqueous solution of potassium chloride contain HCl as well as KCl, and may not the evolution of hydrogen and formation of alkali be due to the decomposition of the HCl?

with a mixture of coarsely crushed gas-coke and finely pulverised manganese dioxide. This result is due to the great electromotive force of the peroxide towards zinc, and to its great depolarising power, combined with the good conducting power of the carbon, which was found by special experiments to balance the great resistance of the manganese peroxide. Lead dioxide is an excellent conductor, and voltaic combinations made with it are far superior in power to those containing manganese dioxide, whether the exciting liquid be nitric acid or solution of sodium carbonate or dilute sulphuric acid, but especially in the last case; their utility is however impaired by the fact that the lead dioxide gradually becomes impure, and the resistance of the combination is thereby greatly increased, an inconvenience which can be remedied only by emptying and cleansing the glasses and their contents, whereas a manganese combination is restored to its former activity simply by scraping the zinc rod (W. Beetz, *Pogg. Ann.* cl. 535).

Electromotive Force. As a unit of electromotive force, Latimer Clark (*Proc. Roy. Soc.* xx. 444) recommends, on the ground of uniformity, that of a zinc-mercury couple excited by a paste formed by boiling mercurous sulphate in a saturated solution of zinc sulphate.

The influence of heat on the electromotive force of voltaic couples has been examined by A. Voller (*Pogg. Ann.* cxlix. 394).

Within the limit 0° – 100° a rise of temperature produces :

a. Increase of Electromotive power in :

Zn in $\text{SO}^{\cdot}\text{H}^2$	About 0.05; below the boiling point a maximum appears to occur.
C in $\text{NO}^{\cdot}\text{H}$	Not very considerable.
Pt in $\text{NO}^{\cdot}\text{H}$	At least equal to that in the last combination.
Cu in NaCl	Considerable and continuous; at 78° the increase amounts to 0.17 of the value at 21° .

β. Diminution of Electromotive power in :

Zn in $\text{SO}^{\cdot}\text{Zn}$	Continuous; at 90° about 0.08 of the initial value at 28° .
Zn in NaCl	Continuous; of the same amount as in the last.
Cu in $\text{SO}^{\cdot}\text{Cu}$	Very considerable; at 91° about 0.43 of the initial value at 22° .
Cu in $\text{SO}^{\cdot}\text{Zu}$	Very considerable; at 80° about 0.33 of the value at 25° .

The general result is that the electromotive force of acids to metals is increased,^c and that of neutral saline solutions to metals (except Cu in NaCl) is diminished by rise of temperature.

temperature
cooling to

creased to at least 25 times its value at ordinary temperatures. In a zinc-carbon cell excited by mercurous sulphate (*1st Suppl.* 554), the internal resistance is increased at -15° to 20 times its ordinary value, while the electromotive force is diminished by only one-tenth. In Leclanché's battery (*1st Suppl.* 555) the resistance is not quite doubled at -18° , while the electromotive force diminishes by about one-eighth.

Electromotive and Thermo-electric Forces of certain Alloys in contact with Copper (H. F. Sandell, *Pogg. Ann.* cxlix. 144).—The method employed for the measurement of these forces was the same as that used by Edlund for estimating the electromotive force developed by the contact of simple metals (*2nd Suppl.* 443), and the main result of the investigation is that the same law holds good for these alloys as for the simple metals, namely, that the order of succession of the several alloys with regard to their electric tension in contact with copper is the same in the thermo-electric as in the voltaic series. The order of tension is given in the following table, in which each alloy is positive with regard to the next. *E* denotes the voltaic, *Θ* the thermo-electric force, *q* the quotient of the two.

Alloy of 12 bismuth with 1 tin	254.74	270.69	1.10
" 8 " " 1 "	234.18	236.39	1.09
" 4 " " 1 "	137.49	146.75	1.06
Iron	82.36	86.12	1.05
Alloy of 2 bismuth with 1 tin	49.76	51.59	1.04
Copper	0	0	—
Nickel-silver	98.08	103.12	1.05
Alloy of 32 bismuth with 1 antimony	295.01	295.24	1.00
Bismuth	417.14	460.06	1.10
Alloy of 32 bismuth with 3 antimony	533.98	680.94	1.29

These results hold good only for temperatures below 30°. The quotients q (except the last) differ from the mean value 1.06 by 6 per cent. at the utmost, the difference being within the limits of experimental error. The difference observed in the case of this last alloy may be ascribed to the circumstance that its very great electromotive and thermo-electric power gives rise to abnormal heat-effects which disturb the action of the apparatus. Lastly it is found that pure bismuth and its alloys with tin exhibit, in course of time, a steady decrease of electromotive and thermo-electric power.

Thermo-electric relations of certain Metals during Fusion and Solidification.—These relations have been investigated by A. v. Obermayer (*Wien. Akad. Ber.* [2 Abth.] lxvi. 63), and by A. v. Fitzgerald-Minarelli (*ibid.* lxxi. 694). The metal to be tested was melted in a funnel, and a wire of the same metal, passing downwards through the neck of the funnel, was soldered to a wire of another metal, the other end of which dipped into the melted metal. The point of junction of the two metals was kept at 0°. Obermayer finds that the thermo-electric relations of metals are for the most part but little affected by fusion or solidification. When the melted metal consists of tin, lead, or the alloy PbSn^3 , and the immersed metal of iron, the electromotive force does not vary at all during fusion or solidification. Zinc, in combination with iron or copper, exhibits nearly constant electromotive power, so likewise does a bismuth-iron couple.

Minarelli has determined the thermo-electric power of the following couples between 0° and 100°, taking that of iron and nickel-silver as the unit :

Iron-tin	0.8999	Bismuth-copper	3.421
Iron-lead	0.9936	Bismuth-platinum	2.720
Lead-antimony	4.403	Bismuth-antimony	5.179
Lead-zinc	0.723	Tin-zinc	0.398
Bismuth-iron	4.274	Tin-antimony	2.677

The curves which represent the results of observation during fusion and solidification, show that a regular variation of electromotive force takes place as the temperature alters through the melting point. The curves for fusion and solidification agree exactly in all cases, excepting for the bismuth-couples, a circumstance which may be due to the difficulty of obtaining this metal in a pure and homogeneous state. The electromotive power of these couples attains its maximum near the melting point of bismuth, and then slightly diminishes. The iron-zinc and tin-lead couples exhibit very slight alterations of electromotive power on both sides of the melting point. The antimony-couples are distinguished by great increase of electromotive force concurrent with rise of temperature.

On the Thermo-electric properties of Potassium and Sodium, see Naccari a. Bellati (*Gazz. chim. ital.* vi. 419; *Jahresb. f. Chem.* 1876, 108).

On the Theory of Thermo-electricity, see Kohlrausch (*Pogg. Ann.* clvi. 601; *Jahresb.* 1875, 96); also O. J. Lodge (*Phil. Mag.* [5], ii. 524).

Electrolysis. Of Hydroxides.—Janeczek (*Deut. Chem. Ges. Ber.* viii. 1018) regards the electrolysis of water as a resolution of H^2O into H and HO, the free oxygen evolved at the anode being a secondary product of the decomposition of hydrogen peroxide, $\text{H}^2\text{O}^2 = \text{H}^2\text{O} + \text{O}$. In like manner it may be supposed that potassium hydroxide is directly resolved by the current into K and OH. When the current is passed through dehydrated potassium hydroxide fused in an open silver capsule, a brisk evolution of oxygen takes place at the anode, whilst at the cathode shining metallic potassium is deposited without evolution of hydrogen. If, however, the decomposition be performed in a closed silver tube, in which the gases can be collected, and the action be continued for some time, the evolved gas is found to be a mixture of oxygen and hydrogen, and water condenses in the delivery tubes. The formation of the water and oxygen is explained by the equations, $\text{KHO} = \text{K} + \text{HO}$, and $\text{H}^2\text{O}^2 = \text{H}^2\text{O} + \text{O}$; and the hydrogen is probably due to the action of the metallic potassium on the undecomposed hydroxide: for, if the heat be continued, its evolution goes on for a long time, even after the interruption of the current; and if, after it has ceased, the melt be thrown into water, no further evolution of hydrogen is observed, whereas it is sure to take place if the melt be cooled immediately after the interruption of the current, and then thrown into water.

From these results, Janeczek infers that the current, in its passage through different liquid compounds, sets free in equal times an equal number of equivalencies, and, therefore, performs in all cases the same amount of work.

2. **Of Alkaline Carbonates.**—From the products obtained by the electrolysis of solutions of neutral and acid sodium carbonate, and the quantities of heat evolved in the operations, Favre a. Roche (*Compt. rend.* lxxviii. 1678) infer : (1). That the

neutral carbonate splits up into CNaO^2 and Na , the sodium being oxidised at the anode with liberation of hydrogen. The group CNaO^2 may be sum-

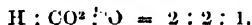
$2\text{CNaO}^2 = \text{C}^2\text{Na}^2\text{O}^2 + \text{O}$, the group $\text{C}^2\text{Na}^2\text{O}^2$ then reacting with water so as to form the acid carbonate: $\text{C}^2\text{Na}^2\text{O}^2 + \text{H}^2\text{O} = 2\text{CNaHO}^2$.

The acid carbonate is resolved by electrolysis into Na and CHO^2 (not, as might be supposed, into H and CNaO^2), the Na being then oxidised, with evolution of hydrogen, while the other product is resolved, in the manner shown by the equation $2\text{CHO}^2 = 2\text{CO}^2 + \text{H}^2\text{O} + \text{O}$, giving rise to the evolution of carbon dioxide and oxygen.

The calorimetric investigation of the thermic changes accompanying these decompositions gave for the neutral carbonate 3772 gram-degrees, the amount required by calculation being 6620; and for the acid carbonate 10445; calc. 12589.

3. Of *Chlorides*.—When a copper-platinum couple is immersed in a solution of cupric chloride, insoluble cuprous chloride is deposited on the platinum as well as on the copper, if the solution be dilute. Zinc-platinum and magnesium-platinum couples give rise to more energetic action, and metallic copper is also deposited on the platinum. Results in harmony with these are obtained with salts of mercury. Again metallic iron reduces ferric to ferrous salts at ordinary temperatures, while platinum by itself has no effect; yet if platinum connected with iron be immersed in the ferric solution, the reduction takes place more rapidly, and the reduced salt forms on the platinum also; or if a little ferricyanide of potassium has been mixed with the solution, the blue colour, which indicates the production of a ferrous salt, will show itself about the platinum as well as about the iron. When plates of magnesium and platinum are immersed in ferric chloride, metallic iron quickly makes its appearance on the platinum plate. With a weak current from a battery passed through platinum electrodes, ferric chloride is resolved into chlorine and ferrous chloride; but with a strong current into chlorine and iron; and this, in conjunction with the facts just adduced, shows the analogy between the electrolysis effected by an external battery and that arising in the cell itself (Gladstone & Tribe, *Phil. Mag.* [iv.], xlix. 425).

4. Of *Formic acid*.—The aqueous solution of this acid yields by electrolysis, at the cathode hydrogen, and at the anode carbon dioxide, with or without admixture of oxygen, but never accompanied by hydrogen. The volumes of the three gases are



The group CHO^2 eliminated at the anode probably reacts with H^2O to form CH^2O^2 and free oxygen, which oxidises the formic acid to CO^2 and H^2O . This view is corroborated by the fact that carbon dioxide is evolved in greater abundance in proportion as oxidation is facilitated by diminishing the strength of the current, increasing the size of the electrodes, and concentrating the acid.

5. Of *Aromatic Bodies*.—When an electric current is passed through an aqueous solution of a aniline hydrochloride, nitrate or sulphate, aniline-black is deposited on the anode, its formation resulting from oxidation of the aniline by oxygen evolved at that part of the circuit (Goppelsröder, p. 69).

The salts of toluidine and pseudotoluidine behave differently from those of aniline. Toluidine-salts give at the anode a brown substance which dissolves in alcohol, and dyes silk and wool brownish-yellow. Pseudotoluidine yields a violet colour, which changes to red on treatment with dilute nitric acid or potassium permanganate. A mixture of aniline, toluidine, and pseudotoluidine gives a red colour, and as secondary product a violet colour. From methyl-aniline a violet colour is formed. Diphenylamine yields a blue product which dissolves in alcohol. A mixture of diphenylamine with ditolylamine and phenyltolylamine gives a beautiful blue colour soluble in alcohol. Methyl-diphenylamine also gives a blue or violet colour.

Phenol in acid aqueous solution, or in the form of phenate, yields a brown compound at the anode. Naphthylamine salts in neutral or acid solution yield naphthylamine violet.

When finely pulverised anthraquinone is added to strong potash-ley, and the liquid, heated nearly to the melting point of potassium hydroxide, is subjected to the action of the current, the part near the cathode becomes first red and then violet from formation of potassium alizarate, which, however, is mixed with brown secondary products of the electrolysis. All these changes depend upon the action of electrolytic oxygen, except the last, which results from that of potassium hydroxide (Goppelsröder, *Compt. rend.* lxxii. 1199).

6. *Oils* and other non-conducting liquids may be rendered conductive and susceptible of electrolysis by mixing them with solutions of metallic salts in alcohol or ether,

e.g. zinc chloride dissolved in alcohol or *Liquor ferri perchlor. fort.* shaken up with ether. Even carbon disulphide may be rendered conductive by such admixtures. The products thus obtained by the electrolysis of oils have as yet, however, been but imperfectly examined (W. Symons, *Pharm. J. Trans.* [3], v. 326).

Electrolysis with Evolution of Hydrogen at both Poles.—If a magnesium wire be immersed in sulphuric acid, diluted to such a degree that only a feeble evolution of hydrogen takes place, and the wire be then connected with a platinum wire likewise dipping into the liquid, the evolution of hydrogen immediately becomes more rapid, and takes place from the surface of both wires, the magnesium at the same time becoming covered with a thin black crust, which disappears as soon as the connection with the platinum is broken. If the two wires, instead of being directly joined, be connected with the poles of a battery, the magnesium forming the anode, exactly the same effects are produced. Whether a battery is employed or not, the quantity of hydrogen evolved at the anode is only half as great as that given off at the cathode, the quantity at the latter being the same as that evolved in an interposed voltmeter. If the electrolyte consists of aqueous magnesium sulphate, in which magnesium does not evolve gas without the aid of the current, the amount of hydrogen evolved at the cathode is likewise nearly double that given off at the anode, and magnesium hydroxide is deposited at both poles, as a powder at the anode, and as a coherent translucent mass at the cathode.

In a solution of potassium sulphate, the same proportion of the gases evolved at the two poles was maintained, and the analysis of the liquids showed that at the anode a quantity of magnesium was dissolved equivalent to the hydrogen liberated in the voltmeter and to the potassium transferred to the cathode; and at the same time a quantity of magnesium equivalent to the oxygen evolved at the anode was oxidised there, but not dissolved.

The evolution of hydrogen at the anode in these reactions is due to the positive electrification of the magnesium, whereby its affinity for oxygen is increased to such a degree that it can take from the water a quantity of oxygen in addition to that which is evolved by electrolysis; but why this additional quantity should be exactly half of that which is due to electrolysis is a question not yet determined (Elsasser, *Deut. Chem. Ges. Ber.* ix. 1818).

A similar effect was observed more than twenty years ago by Wöhler & Buff (*Zamminer's Jahresh. f. Physik*, 1857, 225).

Electrodeposition of Metals.—For obtaining coherent, closely adhering deposits of aluminium, magnesium, bismuth, antimony, and palladium, capable of taking a good polish, A. Bertrand (*Compt. rend.* lxxxiii. 854) precipitates them from the aqueous solutions of their double ammonium chlorides. Aluminium and magnesium require a strong current. Bismuth and antimony may be precipitated from cold solutions, whereas the older methods of precipitating them required the use of hot solutions. Palladium precipitates are easily and quickly obtained, provided the solutions are perfectly neutral. Cadmium precipitates are best obtained from a solution of cadmium bromide slightly acidulated with sulphuric acid, or from an acid solution of the sulphate.

Precipitation of Gold.—Spongy gold employed as an anode in dilute sulphuric acid is quickly and strongly attacked, the cathode at the same time becoming coated with a dark precipitate of gold, and a dark cloud, which deposits a soft black-brown powder, being diffused through the liquid. This precipitate, which is black-blue when dry, consists of gold mixed with a little aurous or auric oxide. Very fine Nobil's rings may be formed by means of a platinum point on gold-leaves immersed in water acidulated with nitric or sulphuric acid. Gold is attacked in like manner, though less strongly, in alkaline liquids. The slightest admixture of silver impairs the beauty of the rings.

Production of Metallic Films on the Surface of Organic Substances by Electrodeposition.—The object to be coated is first immersed in a 10 per cent. solution of silver nitrate in methyl alcohol, to which 3 per cent. of nitric acid is added, and allowed to remain for a longer or shorter time according to its nature. It is then drained, partially dried by rapid motion, and while still moist, placed for a few seconds in a saturated solution of ammonia, after which it is dried at a low temperature. Lastly, it is suspended above the surface of mercury heated by means of boiling water. A few minutes' exposure to the mercurial vapour suffices to reduce the double nitrate of silver and ammonia formed by the previous treatment, the object becoming completely covered with a metallic film.

Leaves, flowers, insects, and other organic objects thus treated, take a regular deposit of copper. The method is said to be safer and more rapid than those in which the hydrogen-compounds of arsenic, phosphorus, and sulphur, or solutions of phos-

phorus in carbon bisulphide are employed as reducing agents (P. Cazeneuve, *Compt. rend.* lxxxii. 1341).

Estimation of Zinc and Lead in Minerals by Electrolysis.—Zinc can be precipitated on platinum in a coherent film, which can be readily washed and weighed if the solution be first rendered ammoniacal and then acidulated with an organic acid, preferably acetic, and submitted to electrolysis, care being taken to adjust the current to the strength of the solution. The iron, lead, &c., present in calamine, blende, and other zinc minerals should be removed by Schwartz's process previous to electrolysis. The presence of a minute quantity of lead greatly increases the coherence of the zinc film, if no mineral acid except sulphuric be present. Lead may be precipitated in a coherent state and of a dull colour by operating on solutions, preferably alkaline, containing phosphoric and tartaric acids. The presence of acetic acid tends to keep the positive pole free from lead peroxide (Parodi a. Mascazzini, *Gazz. chim. ital.* vii. 222).

On the Estimation of Metals by Electrolysis, see also Wrightson (*Zeitschr. anal. chem.* 1876, 297; *Chem. Soc. J.* 1877, i. 340). On the Electrolytic Estimation of Copper and Nickel, see 2nd Suppl. 384 and p. 560 of this volume.

Work of the Electric Current.—From experiments by R. Colley (*Phil. Mag.* [5], i. 469), it appears that when a compound is electrolysed in a long vertical tube, a certain amount of current-force is expended on the mechanical raising of the heavier of the two decomposition-products from the lower to the upper end of the tube, the current being consequently strengthened or weakened according as its direction is in accordance with, or opposed to, that of the heavier of the two constituents of the electrolyte.

Polarisation of Metals. Experiments on the polarisation of several metals have been made by F. C. G. Muller. Amalgamated zinc plates in dilute sulphuric acid gave a very variable polarisation, dependent on the state of the surface of the metal, and the degree in which it was attacked. Clean copper-plates in the same liquid, or in an acid solution of cupric sulphate, exhibited a very regular polarisation increasing with the density of the current; in a neutral solution of cupric sulphate the polarisation is slight, no film of hydrogen being apparently deposited on the cathode, and no water being decomposed simultaneously with the copper salt. In the electrolysis of cupric sulphate with a copper anode, if the smallest quantity of free sulphuric acid is present, cupric oxide is formed on the anode, while on the cathode a deposition of copper takes place without perceptible evolution of hydrogen. Nevertheless, the slight polarisation which takes place in such a case is determined by evolution of hydrogen, arising from the decomposition of the acid: for not only can the hydrogen be smelt, but on reversing the current, the copper oxide deposited on the former anode, now become a cathode, is reduced, and at the same time the polarisation is reduced to nothing, and restored only after complete reduction.

According to Du Moncel (*Compt. rend.* lxxxii. 1022), the difference of the polarisation of electrodes, according as the polarising acids are condensed on the plates, electrolytically or mechanically (*comp. Gauguain, 2nd Suppl.* 444), is observed also when a pebble is interposed between the plates instead of an electrolyte. Peculiar and very irregular polarisation phenomena were exhibited by Franklinite, $\text{Fe}^2\text{O}^3 \cdot \text{ZnO}$, evidently in consequence of its heterogeneous constitution.

Polarisation in Liquids free from Gas.—When a single Daniell's element is connected with a decomposing cell with platinum electrodes, a polarising current is developed, which soon becomes very weak, but does not cease entirely for a very long time. If the Daniell couple be now removed, and the platinum plates of the decomposing cell connected with the galvanometer, a depolarisation current is produced in the opposite direction, strong at first, but soon diminishing, till it becomes almost imperceptible. The apparently unlimited duration of the polarisation current seems at first sight to be inconsistent with the law of the Conservation of Energy. Helmholtz, however, has shown (*Pogg. Ann.* cl. 483) that this current is due to the action of gases—oxygen or hydrogen—occluded in the platinum plates. When an electric current is passed through a water-decomposing cell containing hydrogen, either dissolved in the liquid, or occluded in the platinum plates, the oxygen carried by the current to one of the electrodes will there be reconverted into water by combining with the dissolved or occluded hydrogen. But an equivalent quantity of hydrogen will then reappear at the other electrode, and may be partly dissolved in the liquid, partly taken up by the platinum. A kind of electrolysis is therefore kept up, the products of which do not actually come to light. As this process does not require the amount of chemical work which must be expended when water is ultimately resolved into its elements, it can be kept up by only a weak electromotive force, as long as there remains any dissolved or occluded gas which cannot easily be altogether re-

moved. Helmholtz designates this kind of action by the term 'electrolytic convection.' It likewise takes place when the electrodes and the liquid are charged with oxygen. In a liquid free from gas, and between electrodes free from gas, the polarisation current disappears as quickly as the depolarisation current. In this case the decomposing cell acts exactly like an electric condenser of very great capacity.

According to Fleming (*Phil. Mag.* [5], i. 142), the electrolytic polarisation of platinum plates in dilute sulphuric acid takes place, in the same degree, whether the liquid is aerated or de-aerated. He finds, however, in accordance with Helmholtz, that the polarisation current lasts much longer in liquids charged with gas, than in those which are free from gas.

E. Root (*ibid.* [5], ii. 163) finds that when one side of a platinum plate 0.02 mm. thick, is polarised by electrolytic separation of hydrogen or oxygen, the other side exhibits, after a while, the same state of polarisation, whence he infers that thin platinum plates are *penetrated* by the electrolytic gas. [Is not the gas evolved simultaneously on both surfaces of the plate?]

Polarisation by Chlorine and Hydrogen.—The electromotive force of platinum which has been immersed in hydrochloric acid containing a small quantity of free chlorine, towards pure platinum, is not constant but increases gradually to a maximum. With increasing addition of chlorine it approaches indefinitely to the value of about 0.62 Daniell, but never actually attains that limit. The increase is much quicker from the beginning if the platinum has been immersed in the acid before the addition of the chlorine solution, than when it is immersed in the already chlorinated acid. Hence it appears that the force in question is due altogether to the chlorine condensed on the surface of the platinum, not to that which is contained in the solution; moreover, it appears that the chlorine is attracted by platinum and glass more strongly than by the solution, and that the attraction of platinum for chlorine is about 25 times as great as that of water.

If the chlorine has been liberated by galvanic action, it produces polarisation about 1.7 times stronger than that produced by chlorine prepared by the ordinary chemical methods: hence the active and inactive chlorine are related to one another in the same manner as ozone and ordinary oxygen. The polarisation of platinum charged with ordinary chlorine diminishes between 17° and 100° by 0.062 Daniell; that of platinum charged with active chlorine by 0.449 Daniell. Active chlorine retains its strong electromotive power only in contact with the plate on which it has been produced, and cannot be transferred to another plate by diffusion.

Platinum plates charged with hydrogen in hydrochloric acid solution have an electromotive force, due to polarisation, of 0.68 Daniell, if the hydrogen has been introduced into the solution from without, and of 0.94 Daniell if it has been eliminated on the surface of the plate by electrolysis. Change of concentration acts exactly as in the case of chlorine. With weak currents rise of temperature diminishes the activity. The active hydrogen passes after a short time into the ordinary inactive modification.

Carbon electrodes give similar results, excepting that the polarisation attains its maximum immediately after the closing of the circuit.

Polarisation of Zinc.—According to Overbeck (*Pogg. Ann.* cliv. 445), amalgamated zinc plates immersed in a perfectly neutral zinc solution cannot be regarded as unpolarisable, unless the current is weak; in strong currents, on the other hand, they polarise as strongly as electrodes of pure zinc, and, like the latter, by evolution of oxygen and hydrogen on their surfaces. Their non-polarisation by weak currents may be due to the fact that such currents decompose only the salt, and not the water, and that the addition of a little separated zinc to the amalgam does not sensibly affect the place of the latter in the voltaic series.

Polarisation of Aluminium.—According to Beetz (*Pogg. Ann.* clvi. 456), the polarisation of aluminium plates in dilute sulphuric acid produced by a current of six Grove's elements, is equal to 5.30, and with one element, 1.29, the plate coated with oxygen contributing to the effect more than ten times as much as the hydrogen-covered plate.

It was observed some years ago by Buff (*Liquid's Annalen*, clii. 265), that the great electromotive force of aluminium is due, not only to deposition of oxygen on its surface, but to the formation of a strongly electro-negative layer, which he supposed to consist of silicon. Beetz regards it rather as a suboxide.

Ducrotet observes (*Compt. rend.* lxxx. 280) that a voltmeter formed of a platinum and an aluminium plate in acidulated water, allows the current to pass, only when the aluminium forms the negative electrode, the hydrogen being then evolved on the aluminium plate, and the current having its ordinary strength. On reversing the

connections, the decomposition of water ceases altogether. The surface of the aluminium does not appear to be altered, being protected by a thin film of alumina, on removal of which the polish of the plate reappears.

Electromotive force of very thin Gas-films on Metal plates.—When a voltameter is introduced into the conducting circuit of very rapidly and regularly alternating currents, each individual current eliminates on one of the electrodes an extremely thin film of hydrogen, and on the other a similar film of oxygen, these gases being reconverted into water by the next current which passes in the opposite direction, and consequently disappearing. Nevertheless the polarisation of these very thin films is considerable, the separation even of 0.000000015 mgm. hydrogen, or 0.000000012 oxygen on a square meter of electrode surface, being sufficient to develop an electromotive force equal to that of a Daniell couple. The gases in these very thin films must be regarded as conductors, and the electromotive force between water and platinum as acting through the thin film of gas. As a first approximation the polarisation may be regarded as proportional to the quantity of gas (Kohlrausch, *Pogg. Ann.* cxlix. 97).

Impulsion of Mercury by the Current.—A globule of mercury placed under water or other liquid becomes elongated when an electric current is passed through the layer of liquid in which it is immersed. This impulsion of the mercury is always directed from the pole at which the evolution of gas is strongest, and is entirely due to the mechanical action of the evolved gas, whether the drop lies freely between the two electrodes, or is in contact with one of them. The more complex phenomena which are observed when the mercury is immersed in saline solutions may be explained by the very strong local polarisations developed on the surface of the mercury. When this metal forms the negative electrode, the secondary currents are mostly due to the resulting amalgam. When, on the other hand, it forms the positive electrode, these currents arise from oxidation of the mercury, and reduction of the salts thereby produced by the hydrogen condensed at the negative electrode (Th. du Moncel, *Compt. rend.* lxxvi. 880, 968, 1136).

Electrocapillarity (2nd Suppl. 449). Chemical action between two liquids separated by a capillary partition, is determined mainly by the magnitude of the capillary electromotive force. If this is strong, metals are reduced from their solutions; if it is weak, oxides and other compounds are formed, as in the cases already described. When a cracked tube containing a metallic solution is immersed in a solution of potassium sulphide, metallic copper is soon deposited on the inside of the tube near the crack. But with a solution of potassium hydroxide, which generates a much smaller electromotive force, only gold and silver solutions are reduced, and these but slowly. The same effects are produced with diaphragms of paper or collodion, which are particularly well adapted for the production of oxides. These compounds are obtained from metallic or saline solutions placed in capillary contact with alkaline silicates or aluminates. In a few instances, however, silica and alumina are carried forward by the current, and then form silicates and aluminates. Metallic nitrates thus subjected to the action of potassium aluminate yield crystallised oxides of copper, lead, zinc, cobalt, and nickel. By the action of potassium silicate on calcium acetate, calcium silicate is obtained in small clumps of microscopic double-refracting crystals. From aluminium chloride immersed in potassium aluminate, a crust of double-refracting granules of alumina is deposited. Magnesium aluminate is formed in like manner from magnesium chloride and potassium aluminate. Ferric nitrate immersed in silicate or aluminate of potassium yields ferric hydrate in transparent, red, double-refracting laminae. Manganic nitrate treated in like manner yields crystalline double-refracting lamellae of manganous hydroxide, soon converted into peroxide. Aluminium silicate may be prepared by the action of aluminium chloride on potassium silicate. From potassium dichromate and potassium plumbite, lead chromate is obtained in small orange-yellow double-refracting needles having the composition of melanochroite (Becquerel, *Compt. rend.* lxxix. 82).

Metallic copper, cobalt, platinum, &c., are obtained by reduction in the electrocapillary apparatus when the crack in the glass tube is wide enough to allow the surrounding solution of potassium sulphide to diffuse into the metallic solution in the tube, and thereby produce a precipitate of metallic sulphide, which is then reduced to metal in the capillary fissure. Similar reactions may take place in torn organic tissues.

When a saturated solution of ammonium fluoride is separated by parchment-paper or a collodion film from a saturated solution of calcium chloride, the partition becomes covered on the side of the latter solution with minute crystals of calcium-fluoride, having rounded edges and exhibiting the properties of *hyalophane*. When the liquids separated by the collodion film are cupric nitrate and potassium aluminate,

cupric aluminate is deposited on the side of the latter, in blue crystals apparently derived from a square prism, mixed with crystals of cupric hydrate. If the alumina be replaced by silica, the compound $\text{CuO} \cdot \text{SiO}_2 + 2\text{H}_2\text{O}$ is formed, which occurs amorphous as a natural mineral, called *mountain green* or *copper green*. The artificial crystals appear to consist of oblique prisms and exhibit double refraction. The silicates of zinc, iron, lead, &c., may be obtained by similar methods; also artificial spinel (magnesium aluminate) (Becquerel, *Compt. rend.* lxxviii. 1081).

When a test-tube having a crack in the direction of its length (2nd Suppl. 449) is filled with a strong solution of cupric nitrate, and placed within another tube containing a strong solution of lead oxide in potash, no reduction of copper takes place; but on passing the current of a single Bunsen's or Daniell's cell through the apparatus, the positive copper electrode being immersed in the copper solution, and the negative platinum electrode in the lead solution, metallic copper is deposited after a while on the side of the crack in contact with the copper solution, and lead peroxide on the other side. The nitric acid has therefore combined with the potash, and the liberated oxygen has raised the lead to a higher state of oxidation. The reaction is the same as if the two liquids had been connected by a platinum wire, the crack, in fact, acting like a metallic conductor. Even before the deposition of the metallic copper and lead peroxide, hydrogen and oxygen, proceeding from the decomposition of water, are evolved on the two sides of the crack, the evolution of gas becoming more rapid as the deposit of copper increases and forms an intermediate conductor. All surfaces covered with conducting liquids, and having a capillary layer in close adherence to them, act in the same manner as the crack. A similar but somewhat slower action takes place in the other modifications of the electro-capillary apparatus already described (2nd Suppl. 449).

The electro-capillary apparatus acts with much greater energy when the two liquids separated by the crack are connected together by a syphon-shaped non-capillary tube, through which a wick of asbestos is passed. The liquids which rise by capillary action into the two halves of this wick then come into contact in larger quantity, and act chemically on one another, the metallic solution developing positive, the alkaline solution negative electricity, and the circuit being completed through the crack in the glass (Becquerel, *Compt. rend.* lxxiv. 1310).

Becquerel estimates the electromotive force of an electro-capillary couple as usually equal to three-fourths of that of a Daniell cell; in one case it was found to be five-sixths (*ibid.* lxxvi. 245).

When a metal plate coated with a moist precipitate, metallic or non-metallic, is fixed between two glass plates, to prevent evaporation of moisture, the metal is oxidised at the expense of water which is decomposed, and yields negative, while the liquid yields positive electricity,—each granule of the precipitate surrounded by liquid acting, indeed, like a solid conducting body, and setting up an electro-chemical action. A zinc plate and lead chromate moistened with water yield, after some time, basic lead chromate more or less crystalline, and zinc chromate. Iron instead of zinc, yields, in place of the latter salt, ferric and ferrous-ferric oxide mixed with ferrous chromate and lead chromate. When a saturated solution of copper nitrate is separated by parchment paper from a solution of potassium oxalate, a crystalline deposit of potassium-cupric oxalate is formed on the side of the paper in contact with the latter, while potassium nitrate passes into the copper solution.

Gypsum, kept for a number of years under a solution of potassium carbonate, becomes covered with a crust of crystallised arragonite, formed by the action of electro-capillary currents, which are always produced when a solid body is placed in contact with a liquid capable of acting chemically upon it (Becquerel, *loc. cit.*).

When a solution of potassium dichromate is placed on one side of the crack of the electro-capillary apparatus, and a solution of lead nitrate on the other, slight indications of a current are observed after a few days, and a very small deposit of lead chromate is formed on the side of the lead solution. Lead nitrate and potassium sulphate give a very feeble current, but no precipitate. Other solutions give stronger currents, but still no precipitates. When sulphuric acid ten times diluted is thus separated from sodium carbonate, only a few gas-bubbles are observed after a considerable time, although the current of a voltaic couple easily passes through the crack. In all these cases the chemical and capillary affinities in the crack appear to balance each other (Becquerel, *loc. cit.*).

When the electro-capillary current is strengthened by a current of eight Daniell's cells directed the same way, the following effects are observed: With a solution of alkaline sulphide on the outside of the electro-capillary tube, solution of chromous chloride gives a crystalline precipitate of hydrated chromous-chromic oxide. Ferric chloride gives in like manner a hydrated sesquisulphide of iron. Bismuth chloride gives a precipitate of bismuth sulphide. Lead acetate yields shining metallic lead.

Cupric nitrate gives shining metallic copper on the negative, and crystalline copper sulphide on the positive side. Silver nitrate yields a precipitate of silver sulphide. With zinc chloride and aurous chloride no reaction takes place (Becquerel, *Compt. rend.* lxxix. 128).

When a platinum plate perforated with numerous small holes is laid on each side of the porous diaphragm of an electro-capillary apparatus, and the two plates are connected with the wires of a very delicate galvanometer, this instrument gives no indication of a current, whence Becquerel infers that the current which would otherwise be manifested is neutralised by the electro-capillary current. When, however, the negative plate is connected with the negative pole, and the positive plate with the positive pole of a Daniell's cell, the two electro-chemical actions act in the same direction, and a current is produced.

When an electro-capillary apparatus is filled on both sides with a solution of cupric nitrate, a copper plate connected with the positive pole of a voltaic couple being immersed in the liquid on one side, and a platinum plate connected with the negative pole on the other side, no precipitate of copper is formed on the positive side of the diaphragm so long as there are no traces of copper present on that side, because in that case no electro-capillary current is excited; but if a little copper has been previously deposited on the diaphragm the deposit increases rapidly. Similar effects may be obtained with two liquids as already described (p. 715).

If the sodium sulphide be replaced by caustic potash, and a plate of lead be immersed in the liquid as negative electrode, while lead nitrate is present on the positive side, there are formed on the negative side of the partition a lead-tree and lead oxide, which latter occurs *alone* if the reaction is not assisted by a voltaic battery. Cupric nitrate, with or without the battery-current, yields nothing but blue, crystallised, double-refracting cupric oxide; and if the caustic potash be replaced by the neutral of acid carbonate, hydrated cupric carbonate is formed possessing the same properties (Becquerel, *Compt. rend.* lxxix. 585).

When a strong solution of potassium hydroxide is separated from nitric acid by a spiral roll of parchment paper through which a platinum wire is inserted, an oxygen-couple is formed, inasmuch as oxygen is evolved on the wire which is in contact with the potash, and nitrogen tetroxide on the other. If the nitric acid be replaced by one of the chlorides of iron, or by potassium chloride or cuprous chloride, continuous evolution of gas takes place in a few hours on the portion of the wire immersed in the potash. With chromous chloride, sulphuric acid, and nitric acid, a scarcely perceptible evolution of gas takes place (*loc. cit.*)

With platinum-sponge more or less strongly pressed, as a partition, calcium fluoride is produced from solutions of calcium chloride and ammonium fluoride. When sodium sulphide and nitric acid are the reacting liquids, the oxygen unites partly with the sulphur, partly with the sodium of the former, and nitrogen tetroxide is set free (*loc. cit.*)

Electro-capillary effects are very much weakened by dilution of the liquids. A solution of cupric nitrate fifty times diluted no longer yields metallic copper with a saturated solution of an alkaline sulphide, but only cupric chloride [*? sulphide*] (*loc. cit.*)

When a dilute acid solution and a dilute basic solution are separated by a diaphragm of earthenware, parchment-paper, animal membrane, or cracked glass, an electromotive force is set up which gradually increases—in the case of nitric acid and potash, for example, attaining $1\frac{1}{2}$ times its initial force within two days, while other combinations exhibit a slower increase. As concentrated solutions do not exhibit this gradual increase of power, it is probably due to a capillary attraction between the porous partition and the substances dissolved in the water, which gives rise to a thicker deposition of these substances within the pores of the partition, and consequently to increased electromotive excitation. Dilute salt-solutions exhibit the same effects, but less powerfully (Becquerel, *Compt. rend.* lxxii. 1407).

From a comparison of the electrical and chemical effects which take place in the contact of arterial and venous blood with those observed in the electro-capillary apparatus, Becquerel thinks it may be inferred that the exciting cause in the two cases is the same, and that the capillary system in the animal organism is made up of constant electro-capillary elements. The constancy of the current required for the regular production of hæmatin is insured by the circumstance that this compound continually takes from the arterial blood-corpuscles the oxygen which they carry with them, and transfers it to the inner walls of the capillary veins, which are positive, the oxygen thus transferred serving to oxidise the carboniferous and other bodies which penetrate the walls of the vessels (*Compt. rend.* lxxxv. 1310). The experiments above mentioned (p. 715) in which reduction of copper in a capillary fissure is effected by the aid of a voltaic current, under circumstances in which it

would not otherwise have taken place, may throw some light on the action of a constant current on a muscle (*loc. cit.*)

Function of Water in Chemical Actions.—Becquerel (*Compt. rend.* lxxvii. 84, 1130) has investigated the function of water in the mixing of saline solutions by determining the electromotive forces between water and saline solutions in the electro-capillary apparatus. The electromotive force between the solutions of two neutral salts is always equal to the difference between the electromotive forces of the individual salts towards water. The two latter forces afford evidence of the chemical action of water on the salts; and the equality of their difference to the force resulting from the direct action of the two salts on each other shows that the water in the solution of one salt exerts upon another salt, an action equal in amount to that which the water in the solution of the second salt exerts upon the first. Between a base and an acid, on the other hand, this law does not hold good, the action between the base and acid being considerably less than that of water on the two. Hence it may be inferred that when the solutions of two neutral salts are mixed, the formation of hydrates precedes the occurrence of double decomposition. The same is the case in the mixture of a basic solution with an acid, in which, however, direct double decomposition likewise takes place.

Becquerel has further determined the increase of electromotive force of aqueous solutions of sulphuric anhydride and potassium oxide towards distilled water, consequent on the entrance of 1 mol. more of water into the solution. The proportion between the electromotive force of any one hydrate and that of another containing 1 mol. water in addition diminishes as the total amount of water increases, but approaches indefinitely to a fixed limit.* In the reaction between an acid and an alkaline solution containing equal numbers of water-molecules, the electromotive force stands to that of solutions of the same substances containing one additional molecule of water, nearly in the same ratio, which, however, diminishes slightly as the amount of water increases.

When double decomposition takes place between two salts, as sodium sulphide and cupric nitrate, no current is obtained if water-electrodes (*infra*) are employed, because the electric effects of the two decompositions and combinations are of equal value and opposite sign. It, therefore, we know the electromotive force of Na_2S to H_2O , and that of Na_2S towards the solution of any metallic salt, that of the salt to water may be calculated therefrom. Expressed in hundredths of the electromotive force of a zinc-cadmium couple, that of Na^+ to $\text{AuCl}^- = 462$; to $\text{NiCl}^- = 409$; to $\text{Fe}^+\text{Cl}^- = 384$; to $\text{ZnCl}^- = 319$; to $\text{PtCl}^- = 319$; to $\text{Pt}(\text{NO}_3)_2 = 317$; to $\text{H}_2\text{O} = 268$. In an electro-capillary apparatus the electromotive force of water to a solution of sodium sulphide increases with increasing concentration in such a manner that, as the quantity of anhydrous salt in 100 c.c. increases from 0.50 to 5.77 grams, the electromotive force rises from 200 to 222. On adding to 50 c.c. of distilled water a single drop of a solution containing 0.13 grm. anhydrous salt in 1 c.c. a solution is obtained which exhibits towards pure water an electromotive force = 145 (Becquerel, *Compt. rend.* lxxxi. 803).

In the same way it may be shown that double decomposition takes place between the white and yolk of egg, and between arterial blood and each of these substances.

Becquerel has also determined the electromotive forces between the following substances:

Sorrel-juice and	Lemon-juice	=	52.5
"	Egg-yolk	=	38.5
"	Grape-juice	=	47.5
Lemon-juice and	Egg-yolk	=	10
"	Egg-white	=	51
Grape-juice and	Egg-white	=	19.5

In the several combinations, these organic bodies follow the same laws as saline solutions (Becquerel, *ibid.* lxxxi. 849).

The electromotive force between salt-solutions, or between solutions of acid and alkali, may be measured independently of the formation of hydrates (*supra*) by means of water-electrodes—that is to say, cracked glass tubes filled with distilled water and each containing a depolarised strip of gold or platinum. When tubes thus prepared are immersed in two solutions separated by a partition having a capillary fissure, the hydrate-formations taking place in both directions within this crack neutralise those which take place in the cracks in the two electrodes, and the desired action between the two solutions may therefore be observed without interference. Determinations of the electromotive force of $\text{K}^+\text{O} \cdot 6\text{H}_2\text{O}$ towards H^+SO_4 with 1, 2, 6, 12, 24, 48, and 96 mol. water, show that this force increases up to $6\text{H}_2\text{O}$, and then continually diminishes, but always at a decreasing rate (Becquerel, *ibid.* lxxviii. 89).

The mean values of the electromotive forces thus determined for the reactions of K_2O with SO^2 and N^2O^2 are for the former = 0.32 and for the latter = 0.88 of the electromotive power of the Zn—Cd couple excited by solution of cadmium sulphate (*ibid.* 1169).

Relation between Electro-capillary Action and Endosmose.—In order that one or the other or both of these effects may be produced between two liquids, the following conditions must be fulfilled: 1. The two liquids capable of acting chemically on one another must be separated by a permeable partition, which may be either organic or inorganic. 2. Electro-capillary currents are produced only when the permeability of the partition is not great enough to admit of diffusion or filtration, as in that case precipitates, crystalline or amorphous, would be formed by double decomposition. 3. The permeability must be due to a capillary action sufficient to bring the two liquids in contact, and therefore to enable them to react chemically, whence arises a development of electricity sufficient to produce along the sides of the pores an electro-capillary current capable of effecting electro-chemical decomposition. If the pores are so small that all the liquid which enters them can be electro-chemically decomposed, no endosmose or diffusion takes place. 4. If the pores are larger, part of the solution which enters them remains undecomposed and diffuses to the other side, its passage being accelerated by the mechanical propelling action of the electro-chemical current. 5. In living organisms the conditions for the development of electro-capillary currents appear to be completely satisfied; for no double decompositions take place which can be referred to diffusion. 6. The intensity of the electro-capillary current depends on the chemical attraction between the liquids and on the size of the pores, the diameter of which should be such that all the electricity produced by the contact of the liquids may be utilised for the production of the current. The liquids must be conductors of electricity, and the partitions must not be altered by them either physically or chemically (Becquerel, *Compt. rend.* lxxx. 411).

Wiedemann showed, some years ago (*Pogg. Ann.* lxxvii. 211), that the quantities of liquid carried by electrical osmose through a porous diaphragm in equal times are, *ceteris paribus*, proportional to the strength of the current. This law has been confirmed by W. Engelmann (*Archiv. néerl.* ix. 332), who has further shown that the coefficient of permeability, i.e. the quantity of liquid passing through in a unit of time, depends in great measure on the nature of the diaphragm, being much smaller for vegetable and animal membranes, which become drenched with liquid, than for porous earthenware; greater, on the other hand, for moist than for dry tissues.

Electric Conduction and Resistance. *Temporary Alteration of Electric Conductivity by Extension.*—This effect has been examined by H. Tomlinson (*Proc. Roy. Soc.* xxv. 461), who finds that the increase of electrical resistance in a metallic rod (expressed in fractions of the whole) produced by stretching is exactly proportional to the stretching force, and that, after deducting the increase of resistance due to the more lengthening of the rod, and to the diminution of the transverse section of the path of the current, there still remains a positive increase of resistance, which is greatest in iron and least in brass. This part of the increase must therefore be due to the fact that the extension has increased the distances between the particles of the metal in the direction in which the electricity is moving.

Effect of Motion.—Edlund (*Pogg. Ann.* clvi. 251) has shown, by experiments on water and dilute alcohol, that the electric resistance of a moving conductor is less in the direction of the motion, and greater in the opposite direction, than in a state of rest.

Influence of Temperature on the Conducting Power of Metals.—The electric resistance of all metals increases with rise of temperature, most strongly in iron and steel. In iron, at 180° , it is twice as great; at 430° , four times as great; and at 860° , nine times as great as it is at 0° . In all other metals, the conducting power diminishes more rapidly with increase of temperature, in proportion as the melting point is lower. In iron and palladium the resistance at 0° does not become doubled till the temperature is raised to 450° and 400° respectively, whereas in zinc, cadmium, thallium, and tin, it becomes doubled between 200° and 230° . In alloys the increase of resistance is always less than in the constituent metals (Benoit, *Pogg. Ann.* cliii. 411).

Influence of the Passage of a Current on the Electric Conductivity of Iron and Steel.—The prolonged passage of a current through iron and steel bars increases their resistance slightly (up to 0.001), and more strongly in iron than in steel. The closing and interruption of the circuit give rise to the formation of extra currents, showing that the effect depends upon the direction of the molecular magnets in these metals (Herwig, *ibid.* 115). According to Adams (*Proc. Roy. Soc.* xxiii. 633), the resistance of hard steel is diminished, and that of soft steel and soft iron is increased, by the passage of a current through the bar.

Influence of Magnetisation.—When a bar of hard steel is placed in the axis of a helix of wire, and magnetised by the passage of a current through the helix, its electric resistance is diminished nearly in proportion to the square of the strength of the inducing current. When soft steel or soft iron is magnetised either longitudinally or transversely, its resistance increases nearly in proportion to the square of the strength of the inducing current; with very strong currents, however, the increase of resistance is less than it should be according to this law (Adams, *loc. cit.*)

Influence of Physical State.—Buff (*Liébig's Annalen*, cx. 257) found that many chemical compounds which in the liquid state are decomposed by the current, are capable, when solid, of conducting without decomposition, to a slight extent at ordinary temperatures, and in a higher degree when heated to temperatures below their melting points: such was found to be the case with cuprous chloride, potassium dichromate, lead oxide, and lead chloride. Conversely, compound bodies which are conductors when solid, become incapable of conducting without decomposition when liquefied. E. Wiedemann, on the other hand (*Pogg. Ann.* cliv. 318), finds that the *haloid compounds of lead* do not conduct wholly like metals, but are at the same time electrolytically decomposed, the amount of such decomposition increasing rapidly with rise of temperature.

F. Braun (*Pogg. Ann.* cliv. 161) has determined the conductivity of fused salts in the neighbourhood of their melting points. Putting the conductivity of mercury at 0° equal to 100,000,000, referred to which unit that of the best-conducting sulphuric acid is equal to 7,700, the following numbers are obtained:

PbCl ²	=	32200	
NaNO ³	=	11475	
AgNO ³	=	8688	(the same just solidified = 4120)
NaCl	=	8660	
KNO ³	=	6500	
Na ² SO ⁴	=	3680	
SrCl ²	=	2260	
K ² CO ³	=	2160	
ZnCl ²	=	85.9	(the same just solidified = 8.68).

Between the conducting powers of fused salts and those of their aqueous solutions, no continuous parallelism appears to exist. The former are of the same order of magnitude as the latter, though in most cases considerably larger, the only conspicuous exception being found in zinc chloride. No connection can be traced between the galvanic conducting powers of salts and their other physical properties.

Conductivity of Minerals.—Many minerals, especially amorphous silica, exhibit, when an electric current is passed through them, a certain degree of polarisation, arising from their being thrown into the dielectric state, so that their conductivity is both electrolytic and *electrotonic*. The effects of these two properties are, moreover, complicated by those due to moisture and heat. Similar phenomena are observed in vegetable and animal tissues and in various liquids (Du Moncel, *Compt. rend.* lxxxi. 312, 390, 425). When a current is passed through a pebble held between copper or platinum electrodes, these become polarised, and the pebble itself becomes a source of electricity of shorter or longer duration, according to the duration of the electrification and the nature of the body. The reversal of the polarising current gives rise to peculiar effects not yet thoroughly investigated (Du Moncel, *Compt. rend.* lxxxi. 312, 390, 425; lxxxii. 39).

W. Beetz (*Pogg. Ann.* clviii. 653) has determined the conducting power of manganese-ores and of various kinds of carbon, with the following results, referred to the conductivity of mercury as unity:—

	Manganite	Pyrolusite	Nürnberg Battery Carbon	Stick of Graphite
Specific gravity	4.34	4.66	1.47	2.28
Conductivity	0.0000016	0.000123	0.0017	0.00455
	0.0000026	0.000230		
	Munich Retort coke	Ruhmkorff Carbon plate	Bar of Carbon from Dubouché's Lamp	
Specific gravity	1.72	1.82	1.90	
Conductivity	0.0110	0.0138	0.0288	

From experiments by v. Kobell (*Phil. Mag.* [4], l. 24) it appears that anthracites and coals which have been subjected to the action of interpenetrating fused rocks possess a high degree of conducting power, approximating to that of graphite, whereas coals which have been deposited without disturbance, like the Welsh anthracite, are bad conductors at ordinary temperatures, but acquire considerable conducting power when heated to redness.

F. Braun (*Pogg. Ann.* cliii. 556) has examined the conducting power of numerous well-crystallised metallic sulphides, both natural and artificial, and finds that the resistance which they offer to the passage of the current varies with its direction, intensity, and duration, the variations amounting sometimes to 30 per cent. of the entire value. Different results have, however, been obtained by H. Dufet (*Compt. rend.* lxxxi. 628), at least for iron pyrites, which, according to his observations, conducts exactly like a metal, its conducting power being independent of the direction of the current, and varying by at most 1 per cent. according to its duration. Different specimens, on the other hand, exhibit great diversities of conducting power, according to their internal structure, and the direction in which they have been cut.

Conductivity of Vegetable and Animal Substances.—The electric conductivity of various woods has been examined by Du Moncel (*Compt. rend.* lxxix. 41, 110, 164, 296, 356, 591), who finds that it depends almost wholly on the amount of water contained in them, and therefore varies with the state of the hygrometer more quickly in soft than in hard woods, and in each case agrees approximately with Ohm's law. The experiments, however, exhibited numerous irregularities. By drying and saturating with paraffin, most woods may be rendered good insulators, their insulating power being independent of the hygrometric state of the air. The conductivity of mineral substances, especially bricks, is according to their degree of porosity, strongly influenced by the quantity of moisture in the air; so likewise is that of tissues.

In dry air, woollen stuffs are better insulators than silk; and amongst silk stuffs, black silks, especially the more common kinds, acquire, from the various substances used as dressings, a very high degree of conducting power (*ibid.* 753, 945).

When the electrodes of a battery are pressed from without against the bark of *Rhamnus Alaternus*, a slight deviation of the needle of a galvanometer included in the circuit is observed, diminishing a little after a while, but no polarisation of the electrodes is produced. If, on the other hand, one or both of the electrodes be thrust into the stem, both the current and the polarisation are stronger. The human body, after ten minutes' electrification by means of electrodes applied externally to the wrists, exhibits very strong polarisation currents, and mortification of the skin beneath the electrodes (Du Moncel, *Compt. rend.* lxxxiii. 1236).

Electric Resistance of Selenium.—The electric resistance of this body is considerably diminished by exposure to light, the actinic rays of the spectrum producing the least, the red and ultra-red rays the greatest effect, and the maximum appearing to be nearly coincident with the thermic maximum. This influence of light becomes apparent almost instantly after irradiation; but on removing the light, the electric resistance rises to its normal amount, but at a slower rate (Sale, *Proc. Roy. Soc.* xxi. 283).

The increase of the electric conductivity of selenium thus produced, is attributed by Sale entirely to the influence of light, independently of the heat by which it may be accompanied, although the experiments of Hittorf seem to show that the conductivity is increased by heat alone (*Liebig's Annalen*, lxxxiv. 214). Willoughby Smith (*Deut. Chem. Ges. Ber.* vi. 204) also finds that the electric conductivity of selenium is increased by lamp and candle light, even when the rays have previously passed through coloured glass, and hence infers that the effect is independent of the influence of heat. The same view is taken by the Earl of Rosse (*Phil. Mag.* [4], xlv. 161), who has further shown that the effect of the light varies in the inverse ratio, not of the square, but of the first power of the distance from the source of light, and therefore directly as the square root of the luminous intensity; also that in a moist atmosphere the effect of the light is much weaker, and often actually diminishes after prolonged exposure.

The influence of light on the electric resistance of selenium has been further examined by W. G. Adams (*Proc. Roy. Soc.* xxiii. 636; xxiv. 163). Preliminary experiments showed that the resistance of selenium which has not been exposed to light, increases slowly and regularly in consequence of the heat developed by the current, but diminishes, on the other hand, as the strength of the current is increased. Rise of temperature increases the resistance of selenium not exposed to light; exposure to light diminishes it, but after removal of the light, the resistance returns to its former amount. Exposure to full daylight may diminish the resistance by about one-fourth of its entire amount. By the use of absorbing media, it was found that the dark heat-rays and the chemical rays (violet and ultra-violet) have very little influence, but that the effect increases with the intensity of the light, and therefore attains its maximum in the green part of the spectrum. The flame of a Bunsen burner, in its ordinary state, has but very little effect, but, when rendered luminous by shutting the air-holes, it diminishes the resistance by one-fourth. The flame of an ordinary wax candle, having only $\frac{1}{10}$ the intensity of the bright Bunsen flame, diminished the

resistance by $\frac{1}{2}$; the light of the full moon by $\frac{1}{16}$. Further experiments with the light of a candle and of an Argand lamp showed that the diminution of resistance is directly proportional to the square root of the intensity of the light.

Exposure of selenium to light excites and maintains an electric current. Of three lumps of selenium examined, two showed this effect, while the third did not. The sensitiveness of light is, moreover, different in different parts of the same lump. In general, the current passes from the less to the more strongly illuminated portion; the direction may, however, be reversed in consequence of accidental molecular peculiarities. The effect does not appear to depend on thermo-electricity. When a weak current was passed through pieces of selenium having but little resisting power, the resistance was increased by illumination of the end where the current entered, and diminished by illuminating that at which it went out. In sticks of selenium having great resisting power, this power was always diminished by illumination; and the same effect was observed in lumps in which no current could be excited by illumination alone. These irregularities (and those observed by Siemens, *infra*) may, for the most part, be explained on the supposition that in the cooling of fused selenium, the outermost layers, which cool most quickly, have no time to assume the crystalline structure, like those in the interior. Exposure to light favours the development of this structure, and thereby gives rise, not only to increased conducting power, but also to a prolonged molecular transposition, which shows itself, under certain circumstances, in the form of a current.

The influence of heat on the electric conductivity of selenium has been specially studied by W. Siemens (*Pogg. Ann.* cliv, 117). Selenium, as well as tellurium and carbon, exhibits the property opposite to that of metallic conductors—of conducting electricity better at higher than at lower temperatures. It does not, however, retain this property at all temperatures, but loses it by prolonged heating at 200°, and then behaves to electricity like a metal, that is to say, its conductivity is increased by cooling. This metallic condition of selenium, brought into the crystalline form from the amorphous state by heat, is not however stable; but, during and after cooling, slowly returns to the condition of selenium which has crystallised at lower temperatures, in which state it conducts no longer like a metal, but like an electrolyte. A certain portion of the metallically conducting selenium remains, however, dissolved in the latter modification, its quantity being greater or smaller according to the temperature to which it has been cooled. Hence it appears probable that solid selenium, when heated for some time to 200°, is converted into a third allotropic modification, which is stable only at that temperature, and would be reconverted at lower temperatures into the electrolytically conducting modification, were it not that it is dissolved in and combined with the latter. Hence also may be explained the occurrence of a turning point, beyond which the metallic conduction passes into that which resembles the electrolytic (in being greater at high than at low temperatures), as well as the lowering of this point by time and by fall of temperature. The following are the temperatures and galvanometer deflections observed at intervals of five minutes when a stearite crucible containing a block of selenium was placed in a paraffin bath at 280°:

Time after immersion	5	10	15	20 minutes.
Temperature of the Selenium . . .	80°	162°	200°	215°
Deflection (a)	0.	870	1520	120

As the selenium began to fuse (at 217°) the deflection fell to 70°, and the fused selenium became hotter, first quickly, then more slowly to 300°.

An essential part of the electric resistance of selenium appears to have its seat in the layers bordering on the conducting faces, and these border-layers appear to be electrolytically altered by the current, the metallic selenium being, perhaps, separated from the crystalline, and thereby permanently or transiently converted into the crystalline or the amorphous variety. Hence arise apparently contradictory relations of the conductivity, according to the quicker or slower cooling of the selenium, and according to the direction of the current. See further Adams (*supra*).

The alterations of conductivity produced by heat and light in the various modifications of selenium have also been examined by H. N. Draper and R. J. Moss (*Chem. News*, xxxiii. 1). Amorphous vitreous selenium does not conduct even in very thin layers, and in this state it becomes electric by friction. As the selenium passes into the granular state, the conducting power increases proportionally to the temperature, but at the melting point (217°) it suddenly undergoes a great diminution; the minimum is found at 250°. When amorphous selenium, produced by rapid cooling of the fused granular modification, is quickly heated, it begins to conduct the current between 165° and 175°, and with continually greater facility as the temperature approaches the boiling point of selenium. Draper & Moss have prepared three modifications of granular selenium. The first is a non-conductor and does not acquire

conducting power even on exposure to light; the second conducts moderately well, and is not sensitive to light; the third, intermediate between the other two, conducts moderately well, and is very sensitive to light, its conductivity in flat sticks being increased 75 to 100 per cent. by direct insolation, and 10 to 50 per cent. by exposure to artificial light. One form of granular selenium exhibited an increase of electric conductivity with rise of temperature; another exhibited a decrease, behaving in that respect like a metal.

Tellurium does not exhibit any alteration of conducting power on exposure to light, but its resistance is diminished by heating, and in a greater degree after it has been left for some time in an unwarmed place (Adams, *Proc. Roy. Soc.* xxiv. 163). Exner (*Pogg. Ann.* clviii. 625), on heating a bar of tellurium, observed at first a slight increase of its electric resistance, continuing up to the temperature of 90° (in other bars to about 245°), then a steady diminution up to the highest temperature tried, viz. 200°. As the bar cooled, the resistance increased steadily and very considerably, so that at the temperature of the room it was five or six times as great as at the beginning of the experiment. Repeated heatings showed that the final resistance after cooling had always diminished when the time of cooling was less than in the experiment immediately preceding, and had increased in the contrary case. The greater the difference in the time of cooling, the greater in general was the alteration of conducting power. The cause of these effects appears to be that between 110° and 60°, the hot amorphous tellurium passes by a molecular transformation, which takes some time to complete, into slowly conducting crystalline tellurium. The conducting power of tellurium for two bars (I. and II.), obtained by fusion, was found to be as follows (silver = 100) :

At 200°	I. 0.00351	II. 0.00310
At 50° } after fusion	I. 0.00286	II. 0.00298
} after slowest cooling	I. 0.00435	II. 0.00437

Conductivity of Glass.—W. Beetz (*Pogg. Ann.* 1874, Jubelband 23-32) has determined the electric and thermic conducting powers of three kinds of glass of known composition. The results are given in the following table:

	1	2	3	4	5
	Specific gravity	Melting point	Resistance at 300° in mill. Q. E.	Time of discharging the zinc-electrometer	Heat conducting power
I. White French mirror glass.	2.544	1110°	17746	152	0.04523
II. Bottle-green glass	2.540	1080°	6252	36	0.04456
III. Heavy lead-glass	4.701	700°	66010	0	0.04373

These numbers show that the specific conducting power of the glasses for static electricity, given under 4, bears no relation to the electrolytic conductivity under 3. Lead-glass is, at ordinary temperatures, the best conductor of the three, while as an electrolyte it is by far the worst. The specific conducting power is greatest in the glass which contains the largest amount of metal; the other two, which resemble one another more nearly in composition, are likewise more nearly equal in insulating power. The results show that, contrary to the law laid down by Wiedemann & Franz (*Phil. Mag.* [4], vii. 33; *Jahresb. f. Chem.* 1853, 92), the electric and thermic conductivities of the three glasses do not follow the same law. The most easily fusible glass does not become a conductor even at the lowest temperature.

W. Whitehouse (*Chem. News*, xxi. 265) has determined the electric conductivity of glass (not analysed) of different temperatures. A glass tube $3\frac{1}{2}$ inches long, $\frac{1}{8}$ inch in external diameter, and 0.01 inch thick in the walls, surrounded, inside and out, by mercury, into which the electrodes dipped, gave the following resistances w , in Ohm's, at t° C.:

$t =$	165°	185°	210°	255°	270°	300°
$w =$	229500	100.000	69000	22500	9000	6800

J. Perry (*Proc. Roy. Soc.* xxiii. 468) has investigated the electric conductivity of glass, chiefly with reference to its use in electrometric apparatus. Flint glass was found to be best adapted for the purpose. The dependence of the conductivity on the

temperature is approximately represented by the formula $C = ca^t$, in which c denotes the electric conductivity at 74.4° , C that at $74.4 + t$, and $a = 1.027$.

In connection with these results, W. Thomson (*Proc. Roy. Soc.* xiii. 463) has examined the electric conductivity of heated glass by laying a plate of flat glass between a zinc and a copper plate, and measuring the charge acquired by these two plates. At temperatures from about 55° upwards, these charges were already as great as with liquid electrolytes, but required for their development a certain time, shorter as the temperature was higher. Between 100° and 120°, the final charge was somewhat smaller. Both the metal plates were found, after the experiments, to be thickly oxidised on the side next the glass, and the glass plate itself was clouded. Three smoother plates, on the contrary, exhibited no sign of decomposition.

Conductivity of Water (Kohlrausch, *Pogg. Ann. Ergänzungsband* viii. 1; cliz. 233).—The conducting power of water is extremely sensitive to the smallest quantities of admixed substances, being for the most part increased thereby. The minimum conductivity k (referred to mercury as the unit) of water purified with the most minute precautions, was found to be represented by the equation.

$$k \times 10^{10} = 0.72.$$

By mere standing of the water in a platinum dish under a closely-fitting glass bell-jar, the conductivity was raised to double that amount in 5 hours, to 5 times in 20 hours, and to 40 times in 44 days.

Alcohol gave $k \times 10^{10} = 0.34$; ether, 0.01; stannic chloride, SnCl_4 , gave 0.02 as a superior limit.

Conductivity of Acids.—From experiments by Grotrian (*Pogg. Ann.* cli. 378) it appears that the conducting power of sulphuric acid (SO_4H^+) between 0° and 70° and in aqueous solutions of 5 to 10 per cent., may be very nearly represented by a parabolic formula with three constants ($a + bt + ct^2$), which themselves depend in like manner on the percentage of acid. For hydrochloric acid of specific gravity 1.03 to 1.06, and for temperatures from 0° to 33° , linear formulae are sufficient. The numerical results agree within 1 per cent. of those obtained by Kohlrausch. Nippoldt (*1st Suppl.* 564). A* every temperature there exists a maximum of conductivity for a certain percentage of acid, greater as the temperature is higher, viz. from 30.2 to 35.4 per cent. between 0° and 76° . Hydrochloric acid exhibits smaller differences in the opposite direction. According to Kohlrausch, a. Grotrian (*ibid.* cli. 1, 216), nitric acid behaves with regard to temperature like sulphuric acid, and exhibits a maximum of conductivity for 29.0 per cent. at 0° , and for 30.2 per cent. at 40° . The relation between the temperature-coefficients and the amount of acid present cannot, however, in this case, be represented by a parabolic formula.

Further experiments by Kohlrausch (*Pogg. Ann.* cliv. 233) on the electric conductivity of these and other acids, have yielded the results contained in the following table. The first column gives the quantity of acid in 100 parts of the aqueous solution; the second column the specific gravity s , at 15° for phosphoric acid and the haloid acids; at 18° for the rest; the third column shows the conducting power (K) of the aqueous acid at 18° (mercury = 1), multiplied by 10^8 : therefore $K = k_{18} \cdot 10^8$; the fourth the increment of K for 1° C, divided by k_{18} : therefore $\Delta = \frac{\Delta K}{k_{18}}$.

Solution	<i>s</i>	K	Δ		<i>s</i>	K	Δ
H ₂ SO ₄	Sulphuric Acid.			75	1·6734	1421	291
				80	1·7320	1032	349
1	—	429	0·0112	84	—	915	369
2·5	1·0161	1020	115	85	1·7827	916	365
5	1·0331	1052	121	90	1·8167	1005	320
10	1·0673	3665	128	92	—	1030	295
15	1·1036	5084	136	95	1·8368	958	279
20	1·1414	6168	145	97	1·8390	750	286
25	1·1807	6710	154	99·4	1·8354	80	0·0400
30	1·2207	6912	162				
35	1·2625	6776	170	HBr	Hydrobromic Acid.		
40	1·3056	6361	178	5	1·0322	1789	0·0153
45	1·3508	5766	186	10	1·0669	3327	0·0153
50	1·3984	5055	193	15	1·1042	4630	0·0151
55	1·4487	4280	201				
60	1·5019	3487	213	HI	Hydriodic Acid.		
65	1·5577	2722	230		1·0370	1249	0·0158
70	1·6146	2016	256				

Electric Conductivity of Acids.

Solution	s	K	Δ	Solution	s	K	Δ
HCl	Hydrochloric Acid.			C²H⁴O²	Acetic Acid.		
5	1.0242	3693	0.0159	0.3	—	2.98	—
10	1.0490	5902	157	1	—	5.48	—
15	1.0744	6980	156	5	1.0058	11.47	0.0163
20	1.1001	7132	155	10	1.0133	14.30	169
25	1.1262	6767	154	15	1.0195	15.18	174
30	1.1524	6200	153	20	1.0257	15.04	179
35	1.1775	5535	0.0152	25	1.0325	14.24	182
40	1.2007	4826	—	30	1.0393	13.12	186
				35	1.0445	11.72	191
				40	1.0496	10.13	196
H³PO⁴	Phosphoric Acid.			45	1.0550	8.49	194
5	1.0270	292	0.0100	50	1.0600	6.93	194
10	1.0548	531	104	55	1.0630	5.52	200
15	1.0841	767	109	60	1.0655	4.28	206
20	1.1151	1059	114	65	1.0678	3.17	209
25	1.1472	1315	121	70	1.0685	2.20	0.0210
30	1.1808	1551	130	75	1.0693	1.37	0.0210
35	1.2160	1742	140	80	1.0690	0.76	210
40	1.2530	1884	150	90.7	1.0485	0.0004	0.0210
45	1.2921	1956	161				
50	1.3328	1943	174	C⁴H⁶O⁶	Tartaric Acid.		
55	1.3751	1852	189	5	1.0216	56.2	0.0186
60	1.4208	1717	207	10	1.0464	76.3	191
65	1.4674	1545	229	15	1.0695	87.9	190
70	1.5155	1345	252	20	1.0950	93.4	187
75	1.5660	1132	299	25	1.1211	93.9	192
80	1.6192	917	309	30	1.1484	90.3	200
85	1.6.63	730	350	35	1.1763	83.2	210
87	1.7001	663	0.0372	40	1.2064	73.7	223
				45	1.2360	62.2	242
C²H²O⁴	Oxalic Acid.			50	1.2672	49.9	0.0265
3.5	1.0150	476	0.0142				
7.0	1.0326	734	0.0144				

These numbers, together with the facts previously established by Kohlrausch and Grotthian (p. 723), lead to the following conclusions.

All acids which have been examined in strong solutions exhibit, for a certain proportion of admixture with water, a maximum of conducting power. The acid character of a liquid by no means favours its conducting power.

No simple chemical compound yet examined is a good conductor in the liquid state, but becomes so only when mixed with another, water for example.

The conducting power of sulphuric acid, reckoning from 0 per cent. of acid (pure water) to the anhydride (SO³), begins with a value differing but little from 0°, and ends with the same value, exhibiting in the interval, so far as is yet known, 3 maxima and 2 minima, the latter corresponding with the formulæ H²SO⁴ and H²SO⁴.H²O. The existence of the hydrate, H²SO⁴.2H²O, is not indicated by the numbers obtained. As the temperature rises, the minima and the later maxima disappear. The maximum conductivities of nitric, hydrochloric, and sulphuric acid differ but little from one another, and approximate more and more as the temperature rises.

Aqueous solutions of HNO³, HCl, HBr, and HI have for equal numbers of molecules in the unit of volume, nearly equal conducting powers: whence, in connection with Faraday's law of definite electrolytic action, it may be inferred that, in the electrolysis of these acids under the influence of equal decomposing forces, their constituents are carried past one another with equal relative velocities.

Since the mixture of two non-conducting liquids, as water and acetic acid, produces a conductor, it follows that one constituent of the mixture—the solvent—prevents the ions from too frequent concurrence, and thereby enables them to travel longer distances without reproduction of the original molecules; or, what comes to the same thing, the friction of the electrolytically moving constituents of the compound against the foreign liquid is less than their friction against each other.

Blackrode (*Proc. Roy. Soc.* xrv. 322) confirms the observations of Kohlrausch as to the enormous electrical resistance of simple chemical compounds. He endeavoured to electrolyse carbon disulphide, benzene, stannic chloride, carbon dioxide, hydrochloric, hydrobromic, and hydriodic acid, cyanogen, and zinc-ethyl, all in the liquid state, with the current of 80 Bunsen's cells, also with De la Rue's silver chloride battery of 8040 cells with platinum wires at 2 to 4 mm. distance for electrodes; but in neither of these cases were any decomposition-products obtained, and only in the case of zinc-ethyl, after prolonged action of the current, was an extremely feeble polarisation-current observed. Liquid ammonia, however, forms an exception to the general rule. It is a slightly better conductor and is electrolysed, and with a strong current of at least 80 Bunsen's cells the liquid becomes deep blue and gives off a large quantity of gas, while the positive electrode is blackened. On stopping the current the blue colour disappears. The nature of the blue substance thus produced has not yet been made out.

Conducting Power of Alkaline and Earth-alkaline Chlorides.—The conducting power of these compounds in aqueous solution increases almost uniformly with rise of temperature. For all chlorides in dilute aqueous solution, the temperature coefficients are nearly equal, and as the proportion of salt in the solution increases, these coefficients all at first diminish, those of KCl , NH_4Cl and BaCl_2 continuing to diminish up to the highest degrees of concentration, while those of NaCl , CaCl_2 and MgCl_2 attain a minimum between 10 and 20 per cent., and then again increase. The chlorides of the alkali-metals and earth-alkali-metals do not exhibit any pervading differences in their electric conductivity. It is only on comparing the absolutely best conducting solutions of all the salts (at a fixed temperature, say 18°) that they are found to arrange themselves in the following descending order of conductivity: NH_4Cl , KCl , NaCl , LiCl , CaCl_2 , SrCl_2 , BaCl_2 , MgCl_2 . A maximum of conductivity below the point of saturation is exhibited by CaCl_2 , MgCl_2 , and probably LiCl ; in the rest, the conducting power increases continuously with the concentration, but in various degrees, that of KCl increasing almost exactly in proportion to the concentration. The worst conducting chloride is BaCl_2 , and the best NH_4Cl , which, in a 26 per cent. solution, conducts half as well as the best-conducting acid, and if saturated at 100° would probably equal the latter in conducting power. As the concentration diminishes, the relation of the conducting power to the concentration approaches a limit, the so-called *specific conducting power* of the body in aqueous solution. In the chlorides examined, this limiting value is nearly inversely proportional to the chemical equivalent of the anhydrous salt, and still more nearly proportional to its specific volume (Grotrian, *Pogg. Ann.* cliv. 1, 215).

Relations between the Voltaic Conducting Power and the Friction-constants of certain Saline Solutions.—The temperature-coefficient of the reciprocal friction-constants varies, according to the concentration, in nearly the same manner as that of the conducting power; and variously concentrated solutions of alkaline chlorides of different temperatures but equal friction-constants have a conducting power proportional to their percentage of salt. The influence of temperature is therefore limited to the alteration which it produces in the viscosity of the solution, that is to say, in the power of the liquid particles to push one another aside (Grotrian, *ibid.* clvii. 130, 237).

Electric Resistance of very slowly Conducting Liquids.—The unit of resistance adopted in this investigation was that of a concentrated neutral solution of cupric sulphate. Distilled water does not give constant results, because the smallest quantities of admixed salts produce considerable alterations (p. 723). One sample had a resistance equal to 390, while another, probably purer, exerted a resistance five times as great. Water containing in solution 0.033 per cent. sodium chloride gave a resistance of 5.4, and with an equal quantity of sal-ammoniac a resistance of 40. The resistance of alcohol = 13,000, of ether 40,000; that of carbon disulphide is much greater. The resistance of water (390) sinks, on addition of 0.1 per cent. CdBr_2 to 52; of 0.1 per cent. CuCl_2 to 30; of 5 per cent. CuCl_2 to 1; that of alcohol on addition of 0.1 per cent. CdBr_2 to 1,090; of 0.1 per cent. CuCl_2 to 243; of 5 per cent. CuCl_2 to 25 (Oberbeck, *Pogg. Ann.* clv. 595).

Resistance of Liquids to strong Induction-Currents.—From experiments by Herwig (*Pogg. Ann.* cliv. 81) it appears that the specific resistance of liquids to strong induction-currents becomes smaller, as compared with the resistance of wires, when the electro-motive force of the induction becomes greater, and the transverse section of the liquid and the thickness of the layer are increased. This variation does not depend upon polarisation, which indeed increases with the rapidity with which a given quantity of electricity passes through the apparatus. The equalisation of the two electricities is retarded on their entrance into the liquid, and ultimately takes place

by a kind of discharge. The mixing of alcohol and water, of alcohol and turpentine-oil, and of alcohol and ether, all which liquids are bad conductors when separate, is attended with an increase of conductivity, a result which is in accordance with the observations of Kohlrausch (p. 723).

Electric Conductivity of Gases and Vapours.—A series of experiments has been made by W. Hittorf (*Pogg. Ann.* cxxxvi. 1, 197), showing the great increase of conducting power in gases, caused by rise of temperature, and the very high conducting powers exhibited by the vapour of the alkali-metals as compared with all other gases at the same temperature. In another series of experiments (*Pogg. Ann. Jubelband*, 430), Hittorf has studied the so-called positive unipolarity of flame-gases, which he attributes to a resistance to the transmission of the current at the cathode, which takes place, though in an inferior degree, even in so good a conductor as potassium-vapour. The passage of the spark between the terminals of a circuit may be greatly facilitated by surrounding the cathode with potassium-vapour. According to Herwig (*Pogg. Ann.* cli. 250), the conducting power of mercury-vapour exhibits similar phenomena. This vapour indeed acts, not like a metallic conductor, but like a voltaic arc, and likewise exhibits a resistance to transmission, as well as a difference of behaviour at the positive and negative poles. The resistance of mercury vapour in a tube 4 mm. in diameter between columns of liquid mercury as electrodes, is equal to about 50,000 Siemens' mercury-units.

According to F. Braun, on the other hand (*Pogg. Ann.* cliv. 481), the so-called unipolar conduction of gases, which takes place when the electrodes are introduced into a flame, may be explained by the superposition of two currents, a thermo-current arising from the difference of temperature which generally occurs at the two electrodes, and a contact-current, due to the surrounding of the two electrodes, for the most part, by different liquids. If the latter predominates, a current not exceeding it in electromotive force always meets with less resistance when its direction is contrary to that of the contact-current (and generally also to that of the entire flame-current), than when its direction is the same as that of the latter.

From experiments by Wiedemann and Rühlmann (*Pogg. Ann.* cxlv. 235, 364), it appears that the passage of electricity through rarefied gases always takes place in discontinuous discharges. When equal quantities of electricity are conveyed to the two electrodes, the intervals of time between two successive discharges, and therefore the quantities of electricity required to produce a discharge, increase with augmented pressure, quickly at first, starting from the lowest pressures, then more slowly, and finally nearly in the same ratio as the pressure. Under pressures of 30 to 80 mm. the discharges take place most quickly in hydrogen, then in oxygen, carbon dioxide, atmospheric air, and nitrogen. At very low pressures, however, the order of succession of the last four gases is different, because the influence of the diminution of pressure is not the same in all. Sulphur dioxide behaves almost in the same manner as air.

From further experiments, Wiedemann (*Pogg. Ann.* clviii. 35, 252) infers that the passage of electricity between the particles of gases takes place in the same manner as in a row of electrified balls, two contiguous particles becoming charged by contact with the same kind of electricity, and then repelling one another. If the gas is electrolytically decomposable, the movement of its molecules may be accompanied by a separation, progression and recombination of the ions. When the charge is strong, the velocities, and consequently the temperature, are increased, so that phenomena of ignition may occur.

According to Villari (*N. Arch. Ph. nat.* [2], xlv. 85), the resistance of different gases more or less compressed to the passage of the electric spark, exhibits the following ascending order: hydrogen, nitrogen, air, oxygen, carbon dioxide. Faraday, on the other hand, found the resistance of nitrogen and air to be greater than that of oxygen.

Dispersion of Electricity in Gases.—Warburg (*Pogg. Ann.* cxlv. 578) finds that the rate at which electricity escapes from charged bodies in gases is greatly modified by the influence of the insulating support. When this influence was eliminated, he found that the dispersion of electricity in gases takes place according to Coulomb's law; that is to say, the ratio of the charge remaining after any given time to the initial charge diminishes in geometrical progression. In dry carbon dioxide, and in air, the dispersion is nearly equal; in hydrogen, only half as great as in these two gases. With diminished pressure it decreases considerably, and at 70 mm. in air it is at most only one-third as great as at 760 mm. Damp air does not appear to disperse electricity more quickly than dry air. This result, and likewise the absolute values of the coefficients of dispersion, differ considerably from those generally received on Coulomb's authority, which appear to have been obtained without due regard to the influence of the insulating supports.

The dispersion of electricity in gases has also been investigated by D. Boboulieff (*Sill. Am. J.* [3], vii. 118), on the principles of the dynamical theory of gases, with the following results: (1). The dispersion takes place according to Coulomb's law, as found experimentally by Warburg. (2). The coefficient of dispersion is inversely proportional to the square root of the absolute temperature, and (3) directly proportional to the pressure of the gas. (4). This coefficient depends upon the nature of the gas. The second law is, in a general sense, in accordance with an older result obtained by Matteucci (*Ann. Ch. Phys.* [3], xxviii. 385, 421), according to which the dispersion in dry air increases with the temperature. The third and fourth law have been experimentally verified by Boboulieff. The reciprocal value of the dispersion-coefficient was found to increase, between 760 and 30–50 mm., from 210 to 1700, and in air and hydrogen (under 760 mm.) it exhibited the ratio of 210 to 878. This difference is considerably greater than that found by Warburg.

According to J. W. Fewkes (*Sill. Am. J.* [3], viii. 207), the dispersing power of gas-flames is independent of the size and form of the orifice and of the nature of the substance in which it is made; with unignited gas-streams, however, the dispersion follows different laws.

Dielectric State. Silent Discharge. The term dielectric was employed by Faraday (ii. 399) to denote the electric condition of an insulator placed between two conductors charged with opposite electricities. When the insulator is gaseous, and the charge is strong, a silent discharge of electricity takes place between the two conductors, called by Du Moncel the *condensed electric efflux* (*effluve électrique condensée*). This discharge is capable of inducing powerful chemical reactions, as in Houzeau's ozoniser, or the similar apparatus of Boillot, in which a stream of oxygen is made to pass between two glass surfaces coated with a conducting material, the two coatings being connected with the opposite poles of an induction coil (*2nd Suppl.* 887). A more powerful apparatus for investigating the action of the silent electric discharge on gases has been contrived by A. Thénard (*Compt. rend.* lxxiv. 1280). It consists of three thin-walled glass tubes placed one within the other, the inner cylindrical and the outer annular space being filled with antimony-hydrogen chloride, which is a good conductor, and into this the poles of the induction coil are inserted. The gas passes through the annular space between the middle and inner tubes. If this gas is oxygen, it is quickly converted into ozone. If it consists of carbon dioxide, 300 c.c. of it are decomposed to the amount of 11 per cent. in 16 minutes, 19 per cent. in 56 minutes, 23 per cent. in 176 minutes, and 26.15 per cent. in 337 minutes. If the gaseous mixture is traversed, not by the silent discharge, but by actual sparks, carbon dioxide is reproduced to the amount of 7.6 per cent. (A. Thénard).

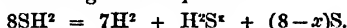
When the gas obtained from pools or marshes, consisting chiefly of methane and carbon dioxide in about equal parts, is passed through this apparatus, it decreases in volume and deposits small drops of a clear oily liquid. The induction-spark, on the other hand, produces in the same gaseous mixture an increase of volume, and a separation of carbon arising from decomposition of the methane. If the gas modified by the spark be afterwards exposed to the silent discharge, it diminishes in volume twice as quickly as before, and yields an oily deposit, the composition of which has not yet been ascertained. On filling the apparatus with 3 vol. hydrogen and 1 vol. nitrogen, ammonia is produced by the action of the silent discharge, but only up to a certain degree of concentration, unless it be neutralised by an acid as fast as it is formed. Acetic acid is decomposed by the silent discharge, giving off carbon monoxide or methane, and leaving a brown oily liquid soluble in potash (P. and A. Thénard, *Compt. rend.* lxxxvi. 517, 983, 1048).

Further experiments by the same authors (*ibid.* 1508) yielded the following results: (1). The electric effluvia can pass through aqueous vapour, decomposing it at the same time. (2). Ammonia gas is also decomposed by it, but, in the absence of an absorbent, only to a certain extent. (3). Nitrogen, in presence of aqueous vapour, disappears, and forms a body which appears to be ammonium nitrite. (4). Phosphine is but imperfectly decomposed, yielding first liquid, then solid phosphide of hydrogen, and finally a body which appears to be amorphous phosphorus. (5). In a mixture of phosphine and ethylene, the electric effluvia gives rise to a substituted phosphine. (6). Methylene monohydrate in presence of water is converted into methane, hydrogen, a strong acid soluble in water, and a resinous body.

A. Boillot (*Compt. rend.* lxxvi. 638, 869), with an apparatus similar to that of Thénard, but with pulverised retort-charcoal as the electrode substance, has found that sulphur-vapour and oxygen, which, when not subjected to electric influence, yield sulphur dioxide and a small quantity of the trioxide, yield, under the influence of the electric discharge, a considerable quantity of sulphur trioxide. Sulphur-vapour and pure hydrogen, which ordinarily do not act on one another, immediately yield hydrogen

sulphide under the influence of the electric effluvium. For the production of *ozone*, atmospheric air appears to be better adapted than pure oxygen, the presence of the nitrogen probably retarding the reversion of the ozone into ordinary oxygen.

The formation and decomposition of binary compounds under the influence of the silent discharge has also been studied by Berthelot (*Compt. rend.* lxxxii. 1283, 1360; lxxxiii. 677, 933). When *nitrogen* and *hydrogen* combine under this influence, not more than 3 per cent. of the gases is ever converted into ammonia, whereas the proportion of ammonia gas decomposed under the same circumstances is likewise 3 per cent. (and therefore 6 per cent. of the original gases). *Nitrogen monoxide* is for the most part decomposed in a few hours, the greater part of the oxygen being absorbed by the mercury; the nitrogen is not re-oxidised. From *nitrogen dioxide* part of the oxygen is separated in the free state, another considerable portion being converted into monoxide. *Hydrogen sulphide* is resolved into hydrogen, a polysulphide, and free sulphur, according to the equation



Hydrogen selenide decomposes in a similar way. *Phosphine* is decomposed according to the equation $2\text{PH}^3 = 5\text{H} + \text{P}^2\text{H}$. The fluorides of boron and silicon, gaseous chlorine and bromine are not altered. *Sulphur dioxide* is decomposed to the amount of one-tenth into oxygen and sulphur insoluble in carbon sulphide. *Cyanogen* is quickly converted into paracyanogen. The decomposition of carbon monoxide yielded the brown suboxide C^4O^2 discovered by Brodie (*2nd Suppl.* 259): $5\text{CO} = \text{CO}^2 + \text{C}^4\text{O}^2$. This oxide is an amorphous substance having the appearance of an extract, and an acid reaction; very soluble in water and in alcohol, insoluble in ether. It forms brown amorphous precipitates with silver nitrate (without reduction), lead acetate, and baryta-water. Heated to $300^\circ\text{--}400^\circ$ in an atmosphere of nitrogen, it decomposes according to the equation $3\text{C}^4\text{O}^2 = 2\text{CO}^2 + 2\text{CO} + \text{C}^6\text{O}^3$, yielding a new dark brown oxide which decomposes at a higher temperature, with formation of an oxygenised charcoal. *Methane*, *ethylene*, and *ethane* yield small quantities of acetylene, together with free hydrogen and resinous hydrocarbons. With *methane*, an odour of turpentine-oil is evolved. With *ethylene*, a liquid product is obtained having the empirical formula $\text{C}^{10}\text{H}^{16}$, together with ethane. Pure *ethane*, on the other hand, yields small quantities of acetylene and ethylene.

Another method adopted by Berthelot for electrifying gases consists in enclosing them in glass tubes coated inside and out, with platinum, and therefore forming small Leyden jars. The inner coating of one such tube was connected with the positive, and that of another with the negative pole of a Holtz machine, the two outer coatings of the tubes being connected together, so that when sparks were passed between the poles, the two tubes were alternately charged and discharged, the one with positive, the other with negative electricity. Oxygen subjected to the action of this apparatus yielded ozone in variable quantity, rather larger with positive than with negative electricity. After twelve hours' electrification, the ozone obtained amounted to 8.85 per cent. of the original quantity of oxygen. By absorbing the ozone with arsenious acid, the whole of the oxygen may be gradually converted into ozone. It is only, however, with strong electric tensions, as with sparks a centimeter long, that these large quantities of ozone can be obtained; with smaller tensions the amount is much less. Compounds of *nitrogen* with *oxygen* could not be obtained in this apparatus either with moist or with dry mixtures of the two gases. But nitrogen, either pure or mixed with oxygen, is absorbed under the influence of the silent discharge, by many organic bodies, either at high or at low tensions. The fixation of the nitrogen is most readily effected by moist filtering paper, less readily by ether, still less by benzene. The products are fixed complex nitrogenous compounds, but neither ammonia nor any acid of nitrogen is formed under these circumstances. The electric tension required to bring about these reactions is not greater than that which frequently exists between strata of the atmosphere not far from the ground, so that we have here perhaps an explanation of the fixation of nitrogen in nature, without previous formation of ozone, ammonia, or nitrous compounds. *Hydrogen* under similar conditions is even more readily absorbed by certain organic substances. Thus 1 c.c. of benzene will take up 250 c.c. of hydrogen, and turpentine-oil likewise absorbs the gas freely. *Acetylene* mixed with hydrogen absorbs a portion of it, yielding various products. The electrified hydrogen does not combine with pure carbon, but a mixture of hydrogen and carbon monoxide yields a solid product and carbon dioxide, together with a trace of acetylene and a hydro-carbon belonging to the paraffin series (see HYDRO-CARBONS).

ELEMENTS. On the Nature of the Chemical Elements, see Casp. Simmen (*Jahresb. f. Chem.* 1876, 4); Baumhauer (*Deut. Chem. Ges. Ber.* vi. 632; *Jahresb.* 1870, 4; 1873, 10); Berthelot (*Compt. rend.* lxxviii. 1352); Groshans (*De la Nature*

des éléments de la Chemie, Haarlem, Leipzig, 1875, 1-109; also *Deut. Chem. Ges. Ber.* v. 625, 689, 754; vi. 519, 523, 704, 1079, 1295, 1354; *Arch. neerl.* 1873, viii. 41; 1874, ix. 193). On the Spectra of Elementary Bodies, see SPECTRAL ANALYSIS.

The idea of a periodic relation between the atomic weights of the elementary bodies and their quantivalence and other properties, developed by Mendelejeff in the manner already described (*2nd Suppl.* 462), was first suggested by J. R. Newlands in 1864 (*Chem. News*, x. 94).

Amyrin, the principal constituent of this resin (according to Flückiger), has lately been examined by E. Buri (*N. Rep. Pharm.* xxv. 193). It occurs in elemi in microscopic prisms which may be separated from the other constituents by treatment with cold alcohol, in which it is insoluble; and by repeatedly crystallising the residue from hot alcohol, the amyrin is obtained in spherical groups of colourless needles having a silky lustre. It is insoluble in water, but dissolves easily in carbon sulphide, ether, and chloroform. 100 pts. of alcohol at 16° dissolve 3.627 pts. of amyrin. Strong sulphuric acid dissolves it with reddish colour; melting potash has no action upon it. A solution of amyrin having a temperature of 16°, a sp. gr. of 0.8255 at that temperature, and a length of 200 mm., turns the plane of polarisation of the yellow ray (sodium line) through an angle of 4.5° to the right.

Amyrin melts at 177°, and does not solidify again till cooled to a much lower temperature. When very carefully heated, it sublimes in long thin needles, but the yield is very small. Dried at 100°, it gives by analysis 83.31 to 83.77 per cent. carbon and 11.39 to 11.81 hydrogen, the formula $C^{20}H^{40}O$ requiring 83.30 C., 11.73 H., and 4.47 O. According to Flückiger, its composition is $C^{20}H^{40}O = (C^{10}H^{20})_2.H^2O$.

Products of Dry Distillation.—Amyrin, heated in a retort, melts and decomposes, giving off at 200° a thin, oily, yellow distillate, which becomes thicker as the temperature rises. On subjecting this liquid to fractional distillation, the temperature rose from 60° to 200°, without giving products of constant boiling point. The following fractions were separated:

The fraction boiling at 60°-70° formed a colourless liquid lighter than water, almost tasteless, and having a pleasant smell; it gave by analysis 83.13 to 83.47 per cent. carbon and 14.50 to 14.75 hydrogen. This portion of the distillate afterwards proved to be a mixture of a body soluble in water, and another which was insoluble. The solution gave iodoform with iodine and potash. The undissolved portion was perfectly tasteless, while the soluble portion gave to the water an aromatic taste and pleasant smell. The former dissolved iodine with a raspberry-red colour, while the original solution, before treatment with water, dissolved iodine with the colour of alcoholic tincture of iodine. The higher-boiling liquids were shaken up with potash, whereby a small quantity (more especially that distilling over between 201°-280°) was dissolved. After the alkaline solution had been acidified and distilled, a colourless watery liquid was obtained, together with a few drops of a yellow oil, smelling like creosote, and dissolving but slightly in water, readily in potash and alcohol. The filtered aqueous solution gave, with ferric chloride, at first a light blue colour, then turbidity with disappearance of colour. With chlorine and bromine-water, a white turbidity was formed. Sodium thiosulphate formed a flocculent precipitate. Mercurous nitrate, after a short time, gave a black precipitate, and nitric acid produced a large quantity of oxalic acid.

The fraction distilling at 185°-200° was a yellow thin liquid, sparingly soluble in water, with pleasant smell and aromatic taste, and giving by analysis 81.65 per cent. C., 11.47 H., and 6.68 O.

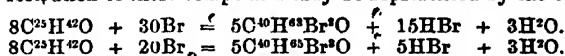
The fraction distilling at 260°-280° was a golden-yellow thick liquid, with slight smell and sharp taste, insoluble in water, and giving 84.40 C., 11.56 H., and 4.04 O.

Above 300°, a thick brown liquid distilled over. The yellow powder observed at the end of the distillation consisted of three different bodies, which could not be separated and purified.

Action of Nitric Acid on Amyrin.—Boiling nitric acid forms with amyrin a clear yellow solution, which, after evaporation, leaves a yellow mass. This mass gives an acid solution in water, as it contains oxalic acid. It reduces Fehling's solution when warmed. The greater part, however, is not soluble in water; it forms a resin-acid, which, when boiled with alcohol, deposits a yellow powder on cooling. Dry hydrochloric acid gas does not act on amyrin, either alone or dissolved in chloroform.

Action of Bromine.—Bromine acts very strongly on solid amyrin, forming a blackish-green mass, with strong evolution of hydrobromic acid. A cold saturated alcoholic solution of amyrin, treated with an excess of bromine, deposited after several hours a yellow precipitate which, when recrystallised from hot alcohol, formed a colourless indistinctly crystalline powder, melting with decomposition at 130°.

The analysis of this body gave 29.82 to 30.10 per cent. bromine, 59.58 to 59.67 carbon, and 7.95 to 8.17 hydrogen, numbers which may be represented approximately by either of the formulae, $C^{40}H^{63}Br^{10}O$ and $C^{40}H^{65}Br^{10}O$, the former requiring 60.07 per cent. C., 7.89 H., 30.04 Br., and 2.00 O., the latter, 59.93 C., 8.11 H., 29.96 Br., and 2.00 O. The formation of these compounds may be represented by the equations:—



Acetyl-amyrin, $C^{28}H^{41}(C^2H^3O)O$, is formed by heating amyrim to 150° in a sealed tube for several hours, and is obtained by crystallising the product from hot alcohol, in white micaceous laminae. It melts at 198° , and solidifies at a few degrees lower. It is less soluble in alcohol than amyrim, 100 pts. of alcohol at 18° dissolving 0.473 pts. of it. Its analysis gave 80.71 to 81.23 per cent. C., and 10.90 to 10.97 H., the formula $C^{27}H^{44}O^2$ requiring 81 C., 11 H., and 8 O.

The crystallisable resin of elemi, insoluble in cold alcohol, analysed by H. Rose, Hess, Johnston, and others (ii. 482) is doubtless identical with amyrim, though the melting point (149°) found by Johnston seems to show that his product was impure.

Brean, from icia or incense-resin, the produce of the *Hyawa* or Incense-tree of British Guiana, and masopin, from the *Dechille*, a tree growing in Mexico, agree very nearly in composition with amyrim; but their melting points are lower than that found by Buri for amyrim, brean melting at 105° , and masopin at 165° (*Gmelin's Handbook*, English Edition, xvii. 421, 422).

Icacin, the crystalline resin lately obtained by Stenhouse and Groves from icia resin—which they regard as a variety of elemi—bears a great resemblance to amyrim. Stenhouse and Groves assign to it the formula $C^{46}H^{70}O$, but Buri supposes that it may have the composition $C^{46}H^{70}O = (C^9H^{14})^2.H^{2}O$, analogous to that of amyrim.

Bryoidin. This substance, originally described by Baup as a constituent of arbol-a-broa resin (i. 354), has also been obtained by Flückiger (*N. Rep. Pharm*) from elemi. The resin is exhausted with spirit of 22 per cent., the extract recrystallised from spirit of the same strength, then distilled with water to remove essential oil, and the remaining resin is extracted with hot alcohol, whereby the crystallisable resin (amyrim) is separated from the amorphous resin, the former crystallising out on cooling, while the latter remains dissolved in the alcohol.

Pure bryoidin crystallises in shining prisms, melts at 135° – 136° , sublimes easily, dissolves in alcohol, carbon sulphide, chloroform, ether, acetic acid, elemi-oil, and glycerin, and sparingly in water. Dry hydrochloric acid gas turns it first red, then violet blue, and green, the mass at the same time becoming liquid. Flückiger's analysis leads to the formula $2C^{10}H^{16} + 3H^{2}O$.

According to Flückiger, the constituents of elemi form the following series:

Essential oil	$C^{10}H^{16}$
Amyrim	$2C^{10}H^{16} + H^{2}O$
Amorphous resin.	$2C^{10}H^{16} + 2H^{2}O$
Bryoidin	$2C^{10}H^{16} + 3H^{2}O$

ELLAGENE. See the next article.

ELLAGIC ACID, $C^{14}H^{10}O^2$. On the formation and constitution of this acid, and its relations to tannic acid, see TANNIC ACID (2nd Suppl. 1143).

Derivatives of Ellagic Acid (Rembold, *Deut. Chem. Ges. Ber.* viii. 1494).

1. Ellagene, $C^{14}H^{10}$, is formed when ellagic acid is heated to low redness with zinc-dust, and passes over first as a colourless distillate, solidifying in laminated masses, which melt at 88° and begin to boil at 252° . This substance dissolves in glacial acetic acid, benzene, ether, and alcohol, forming solutions which are not fluorescent. In a current of hydrogen it begins to sublime at 60° . Analysis of the body and a determination of its vapour-density show that it is a hydrocarbon of the formula above given. It is therefore isomeric with phenanthrene (and with tolane and anthracene), from which it differs, however, in melting and boiling points. Unlike phenanthrene it is not attacked by chromic or picric acid.

Ellagene is accompanied, towards the end of the distillation of ellagic acid, by a red body, which solidifies as an amorphous, translucent, brittle mass, softening at 65° – 70° , and boiling above 360° . This substance appears to be polymeric with ellagene, since it is always formed in the distillation of that body, and has the same percentage composition. It dissolves in the same liquids as ellagene. The solution in benzene is fluorescent.

2. Rufo-hydro-ellagic acid, $C^{14}H^{10}O^2$, is formed, together with an unstable substance not yet analysed, when ellagic acid in alkaline solution is heated with

sodium-amalgam. The latter body is easily soluble in water, and gives a dirty brown coloration with ferric chloride; rufo-hydro-ellagic acid is less soluble. Both are taken up by ether from the alkaline liquid in which they are formed.

Rufo-hydro-ellagic acid forms colourless crystals melting at 300° , but previously undergoing alteration. It dissolves in alcohol and water; the aqueous solution soon acquires a dirty colour in the air. It is distinguished from ellagic acid, and from other hydro-derivatives, by giving, with ferric chloride first a green, then a wine-red coloration, changing to brown in the air. When dried at 160° , it appears to have the composition $C^{14}H^{10}O^4$. It is easily oxidised by alkalis. Heated to 100° with acetyl chloride, it yields a product which appears to be the diacetyl-derivative.

3. Glauco-hydro-ellagic acid, $C^{14}H^{10}O^7$, is formed by the further action of sodium-amalgam on the brownish residue left on evaporating the ethereal solution of the two bodies above mentioned. It crystallises in greenish-yellow silky needles soluble in alcohol, and gives, with ferric chloride, first a blue, then a green coloration.

ACID, $C^{14}H^{10}O^{10}$ (J. Löwe, *Zeitschr. Anal. Chem.* 1875, 35). This acid, differing from gallotannic acid by addition of 1 atom of oxygen, is contained in Divi-divi and in Myrobalanas, the fruits of several species of Terminalia growing in India. The acid prepared from divi-divi pods dries up over sulphuric acid to a brownish, amorphous, fissured, easily splitting mass, which may be triturated to a yellowish powder. After prolonged drying over sulphuric acid or at 100° , it has the composition above given. Its lead salt precipitated from the alcoholic solution of the acid by a hot alcoholic solution of lead acetate, washed with alcohol, and dried at 100° , has the composition $2C^{14}H^{10}O^{10} \cdot 5PbO$.

The acid does not exhibit any striking characters with reagents; it precipitates gelatin, albumin, alkaloids, and tartar-emetie; gives with lead-acetate a greyish-yellow, with iron acetate a nearly black, and with cupric acetate a light-brown precipitate. Its most characteristic property is the ease with which it is converted into ellagic acid, from which it differs by the elements of 1 mol. water [2 mols, according to Löwe, who represents ellagic acid by the formula $C^{14}H^{10}O^8$]. On heating its solution in presence of the smallest possible quantity of air in sealed tubes placed in a salt-bath, the liquid becomes turbid after two hours, and deposits after several days a copious brown precipitate of ellagic acid, which, by washing with hot water and hot alcohol, is converted into a light-yellow powder. Löwe inclines to the opinion that the ellagic acid formed, together with gallic acid, by heating gallotannic acids with dilute acids (ii. 766), is due to a contamination of the gallotannic acid with the acid $C^{14}H^{10}O^{10}$; for, according to his observations, pure gallotannic acid does not yield a trace of ellagic acid.

ELM TANNIN. See TANNIN.

EMANATIONS. See GASES, VOLCANIC.

EMERALD. See BERYL (p. 323).

EMERYLITE. A variety of margarite, accompanying the corundum of North Carolina. Composition, SiO^2 32.41, Al^2O^3 51.31, CaO 10.98, Na^2O 2.43, H^2O 2.13 (J. L. Smith, *Sill. Am. J.* [3], vi. 184).

EMETINE (A. Glenard, *Compt. rend.* lxxxi. 100). The solution obtained by treating ipecacuanha with cold water containing sulphuric acid yields, when mixed with excess of lime, a precipitate containing emetine, which may be dissolved out by ether. On evaporating the ethereal solution to dryness, treating the residue with acidulated water, and the solution so obtained with ammonia, the emetine is precipitated almost colourless, and much nearer to purity than the product obtained by the ordinary method.

When water acidulated with hydrochloric acid is used to remove the emetine from the ethereal residue, the solution, on evaporation, yields crystals of emetine hydrochloride, which may be obtained pure by recrystallisation, and yield perfectly pure emetine.

Emetine decomposes ammonium chloride—a property also possessed by quinine.

Emetine and its hydrochloride, dried at 110° , have the following centesimal composition:—

	C	H	N	O	Cl
Base	72.25	8.61	5.36	13.78	—
Hydrochloride	63.00	8.15	4.75	11.64	12.46

These numbers lead to the formulæ $C^{20}H^{14}N^2O^4$ and $C^{20}H^{14}N^2O^4 \cdot 2HCl$. According to J. Lefort and F. Wurtz, on the other hand (*Compt. rend.* lxxxiv. 1299), emetine has the formula $C^{20}H^{10}N^2O^3$, and its nitrate $C^{20}H^{10}N^2O^3 \cdot NO^3H$; but as no analytical

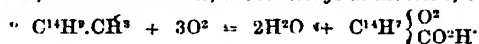
numbers are given in the paper just cited, it is impossible to say whether the base is supposed to contain 3 or 5 atoms oxygen.

Detection.—A trace of emetine brought in contact with chlorinated lime, preferably acidified with a weak acid to liberate the hypochlorous acid, gives a bright orange or lemon-yellow coloration. A few drops of a solution of 1 part of emetine in 1000 parts of water, when evaporated to dryness, readily produce the coloration, and the colour is still perceptible with a solution containing 1 part of the alkaloid in 5000 parts of water. The reaction is well adapted as a means of detecting emetine in forensic analysis, and of testing the value of the various species of *ipecacuanha*. Emetine can be very easily isolated from complicated organic substances by amyl alcohol, chloroform, benzene, and petroleum-benzin in an alkaline solution (F. B. Power, *Pharm. J. Trans.* [3], viii. 344).

Estimation in *Ipecacuanha*.—15 grams of *ipecacuanha* powder are treated with 15 drops of dilute sulphuric acid, and so much alcohol (85 per cent.) as to make the volume up to 150 c.c. After 24 hours, 100 c.c. of the filtered liquid are evaporated until the alcohol is driven off, and the liquid is titrated with standard potassium-mercuric iodide solution, prepared by dissolving 13.546 grams of mercuric chloride and 49.8 grams of potassium iodide in 1 litre of water. 1 c.c. of this solution precipitates $\frac{1}{10000}$ th part of the equivalent of emetine. The final point in the titration is determined by filtering a few drops of the solution containing emetine into a watch-glass placed on black paper, and adding a drop of the standard solution. Not the slightest turbidity should appear if the reaction is at an end. The number of cubic centimeters used is to be multiplied by .0189, i.e. by the $\frac{1}{10000}$ th part of the equivalent of emetine (Zinoffsky, *ibid.* iii. 442).

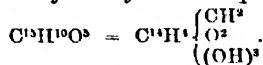
EMODIN, $C^{15}H^{10}O^3$. This constituent of rhubarb-root, discovered by De la Rue a. Müller (ii. 485), is obtained in small quantity, together with chrysophanic acid, by exhausting the root with benzene. Several analyses of it have been published, but its constitution has not hitherto been satisfactorily made out. Now Liebermann finds that, when heated with zinc-dust, it yields about a fourth of its weight of a hydrocarbon much resembling anthracene in its mode of sublimation and crystallisation, also in solubility and the character of its picric acid compound, but melting at 205° like somewhat impure anthracene, and yielding by oxidation with chromic acid a white compound, convertible by heating with strong sulphuric acid into a sulpho-acid which when fused with potash gives the reaction of alizarin. These reactions might lead to the conclusion that emodin is an anthracene derivative, in fact trioxanthraquinone, isomeric with purpurin, $C^{14}H^8O^3$; but the white substance formed by oxidising the hydrocarbon above mentioned with chromic acid, differs from anthraquinone in being partially soluble in ammonia, the solution when mixed with hydrochloric acid depositing an acid compound in white gelatinous flocks. The residue insoluble in ammonia yields by oxidation a fresh quantity of this acid, but the conversion is never quite complete, a small residue being ultimately left consisting of anthraquinone.

The acid thus formed is anthraquinone-carbonic acid, $C^{14}H^8O^2.CO^2H$, and its formation by oxidation of the hydrocarbon obtained from emodin shows that this hydrocarbon consists, not of anthracene, but of methyl-anthracene, $C^{15}H^{12} = C^{14}H^9.CH^3$:



The anthraquinone-carbonic acid thus obtained melts at 280° , sublimes without decomposition, and dissolves in alkalis, the solution, on addition of a slight excess of potash or soda, depositing the alkali-salts in flocks. The acid is in fact identical with that already described (p. 113).

Emodin is therefore a derivative, not of anthracene, but of methyl-anthracene, and its constitution is that of a trioxymethyl-anthraquinone,



This formula agrees well with the published analyses of emodin, viz.:

	De la Rue a. Müller		Rochleder		Skraup		Liebermann		Calculated for $C^{15}H^{10}O^3$
Carbon . .	66.69	66.57	66.63	60.47	65.89	66.05	66.80	66.67	66.67
Hydrogen .	4.07	4.13	4.29	4.27	3.93	4.04	3.93	3.80	3.70
Oxygen . .	29.24	29.30	29.08	29.26	30.28	29.91	29.27	29.53	29.63

The composition of emodin thus established indicates its analogy to chrysophanic acid, which, as shown by Liebermann a. Fischer (p. 470), is a dioxymethyl-anthraquinone.

Liebermann & Waldstein (*Deut. Chem. Ges. Ber.* ix. 1775) have obtained emodin from the bark of *Rhamnus frangula*.

ENARGITE, $3\text{Ca}^2\text{S}.\text{As}^3\text{S}^3$. This mineral, usually regarded as rare, is found somewhat abundantly in the granitic formation of Southern Utah, sometimes associated with octohedral pyrites, and occurring both massive and in brilliant orthorhombic crystals sometimes 5 or 6 mm. long. Combination $\infty\text{P} . 0\text{P} . \infty\text{P}\infty . \infty\text{P}\infty$. Sp. gr. 4.861 in fragments, 5.11 solid, which is somewhat higher than that of the Peruvian variety (analysis *a*). In other parts of the same formation, enargite occurs in broad laminated masses, associated with calcite, and quite free from pyrites and antimony (Silliman, *American Journal of Science*, [3], vi. 126).

Enargite occurs also in the clay slate of the *Sierra de Famatina* in the Province la Rioja of the Argentine Republic, in radio-laminar or granular masses, often alternating with layers of iron pyrites, and forming the principal part of the vein. It is but rarely crystallised, exhibiting in that case the combination $\infty\text{P} . 0\text{P}$, often united in twins, the face of combination being parallel to ∞P . Cleavage perfect parallel to ∞P . Iron-black, often with a steel-blue tarnish on the crystalline faces, and bright metallic lustre.

An antimonial variety of enargite, called *Famatinite*, is found in the same locality, usually massive and imbedded. Sp. gr. = 4.39–4.59; hardness = 3.5 (Stelzner, *Jahrb. f. Min.* 1874, 537).

The following are analyses of those minerals: *a*. Enargite from Utah, analysed by Dana. *b*. Enargite from the Famatina range. *c*. The same, with deduction of the matrix. *d* and *e*. Famatinite.

	S	As	Sb	Cu	Fe	Zn	Pb	Au	Matrix	
<i>a</i> .	34.35	17.20	0.95	46.94	1.06	—	—	—	—	= 100.50
<i>b</i> .	29.92	16.11	2.44	46.38	1.18	0.43	0.68	0.18	2.68	= 100
<i>c</i> .	30.74	16.55	2.51	47.65	1.22	0.44	0.70	0.19	—	= 100
<i>d</i> .	29.28	4.05	20.68	44.59	0.81	0.59	—	—	—	= 100
<i>e</i> .	29.05	3.23	21.64	45.39	0.57	0.59	—	—	—	= 100.47

- The formula of famatinite deduced from the last two analyses is $4(3\text{Cu}^2\text{S}.\text{Sb}^3\text{S}^3) + (3\text{Cu}^2\text{S}.\text{As}^3\text{S}^3)$, whence it may be regarded as an antimonial enargite having one-fourth of the antimony replaced by arsenic.

Another cuprous sulpharsenate called *Luzonite*, dimorphous with enargite and apparently isomorphous with famatinite, occurs in the copper veins at Mancayan in the district of Lepanto in the Isle of Luzon, usually in crude masses exhibiting a structureless, uneven fracture, and a slight tendency to cleavage, perceptible only under strong illumination. In some cavities were found extremely small individuals of unrecognisable crystalline form. Colour dark reddish-grey, gradually acquiring a violet tarnish. Opaque. Hardness = 3.5. Sp. gr. (mean) = 4.2. Brittle, with slight tendency to mildness. The appearance is deceptively like that of famatinite, but differs considerably from that of enargite. An analysis by C. Winckler gave

Cu	Fe	As	Sb	S
47.51	0.93	16.62	2.15	33.14 = 100.26,

which is essentially the composition of enargite (A. Weisbäch, *Jahrb. f. Min.* 1874, 975).

A mineral intermediate between famatinite and luzonite occurs at Cerro de Pasco in Peru. It is associated with enargite and iron pyrites, and could not be completely separated from the latter. The mean result of several analyses is given under A, and the corrected value, after deduction of 13.77 per cent. FeS_2 , under B.

	Cu	Fe	Sb	As	S
A (found)	41.11	6.43	10.93	7.62	33.46 = 99.55
B (corr.)	47.93	—	12.74	8.88	30.45 = 100

(Frenzel, *Jahrb. f. Min.* 1875, 679).

ENSTATITE. This mineral occurs in the bed of magnetic iron ore of the Tilley-Foster mine, Putnam Co., New York. Sp. gr. = 3.29. The following analysis is by E. S. Breidenbaugh (*Sill. Am. J.* [3], vi. 217).

SiO_2	Al_2O_3	FeO	MnO	MgO	CaO	K_2O	Na_2O	H_2O
54.17	3.30	9.94	0.24	31.99	0.99	0.16	0.32	0.13 = 101.24

Decomposed enstatite is found in crystals accompanying apatite on the south coast of Norway. Usual combination, ∞P , $\infty\text{P}\infty$, $\infty\text{P}\infty$, $\text{P}\infty$. Hardness = 2–3. Colour, leek-green. Lustre resinous. Two specimens were analysed: *a*. from Oedegarden; *b*. from Enden:

	SiO ²	Al ² O ³	MgO	FeO	CaO	H ² O	
a.	57.63	1.02	30.37	4.99	—	7.21	= 101.22
b.	59.57	0.97	30.89	2.95	0.37	6.01	= 100.76

The crystals of enstatite often occur associated with undecomposed minerals, sometimes enclosing them, sometimes enclosed by them (Brögger a. Reusch, *Jahrb. f. Min.* 1878, 196).

Brögger a. vom Rath (*ibid.* 1877, 199) have also examined enstatite crystals occurring in a normal apatite vein penetrating the mica and hornblende-slate in the apatite mine of Kjørrestad, between Krageroe and Langesund. Near the normal vein, at Haukdalsvand, there occurs a large isolated mass, consisting almost entirely of enstatite and rutile (with only a trace of apatite), the enstatite crystals sometimes attaining a length of 38 c.m., a breadth of 26 c.m., and a thickness of 13 c.m. One crystal was 40 c.m. in length, but broken off at both ends. The crystals are enveloped in white or greenish talc, and are prismatic, being a combination of the primary prism with a strongly-developed macropinacoid and a narrow brachypinacoid; but a great variety of distortions occur, the brachydiagonal in some cases having the appearance of a clinodiagonal: others again exhibit a true rhombic character, and closely resemble the enstatite of Breitenbach, and the hypersthene from the Rocher du Capuzin in the Mont d'Or and from Laach. The primary pyramid of enstatite from Breitenbach and hypersthene from Laach furnished the following interfacial measurements:

	Enstatite from Breitenbach	Hypersthene from Laach
Macrodiagonal edge	125° 52'	125° 58½'
Brachydiagonal edge	127° 36'	127° 38½'
Lateral edge	78° 42'	78° 34½'

whence $a : b : c = 0.97016 : 1 : 0.57097$.

Only the cleavage angle (prism) of the Kjørrestad crystals could be measured by the reflecting goniometer, and was found to vary from $91^{\circ} 25'$ to $91^{\circ} 40'$, a measurement closely agreeing with the corresponding angles of enstatite from Breitenbach ($91^{\circ} 44'$) and hypersthene from Laach ($91^{\circ} 44'$). The following forms were observed in combinations on enstatite from Kjørrestad, viz.: ∞P , $\infty \bar{P}$, $\infty \bar{P}\infty$, $0P$, $\bar{P}2$, $\frac{2}{3}P\infty$, $\frac{2}{3}\bar{P}\infty$, $\frac{2}{3}P\infty$ and $\frac{2}{3}\bar{P}\infty$; the last four being new.

Kjørrestad enstatite generally has a steatitic outer surface, a complete prismatic cleavage, and an incomplete brachydiagonal cleavage. Sp. gr. 3.153. According to Descloizeaux, the optical axes lie in the brachypinacoid, the acute positive bisectrix being parallel to the edge of the vertical prism. Chemical composition:

SiO ²	Al ² O ³	FeO	MgO	H ² O	
58.00	1.35	3.16	36.91	0.80	= 100.22

ENYSITE. A mineral occurring at St. Agnes in Cornwall, in bluish-green stalactites, having a sp. gr. of 1.59, and giving by analysis:

SiO ²	SiO ²	Al ² O ³	CaO	CuO	CO ²	H ² O	
8.12	3.40	29.85	1.35	16.91	71.05	39.42	= 100.10

These numbers agree with the formula $\text{CuSO}_4 \cdot \text{CuH}^2\text{O}_2 \cdot 3\text{Al}^2\text{H}^2\text{O}_6 \cdot 12\text{H}^2\text{O}$ (J. H. Collins, *Jahrb. Min.* 1876, 868).

ROSIN. This name is given to a beautiful roseate dye-stuff (färs), having the composition of tetrabromofluorescein, $\text{C}^{20}\text{H}^2\text{Br}^4\text{O}^3$, and producible by the action of bromine on fluorescein dissolved in acetic acid (see FLUORESCIN).

EPICHLORHYDRIN, $\text{C}^2\text{H}^3\text{ClO} = \text{CH} \begin{smallmatrix} \text{CH}^2\text{Cl} \\ \text{CH}^2 \end{smallmatrix} > \text{O}$. In preparing this compound by

the action of potash on dichlorhydrin, a loss of material is apt to occur, in consequence of the product aggregating with the simultaneously formed potassium chloride into a pasty mass. This, however, may be prevented by conducting the reaction in a retort, the heat generated being sufficient to drive over a great part of the epichlorhydrin. The remainder may then be distilled off in the ordinary way, but the temperature should not exceed 130° , otherwise decomposition sets in (E. W. Prévost, *J. pr. Chem.* [2], xii. 180).

Epichlorhydrin, treated with sodium ethylate free from alcohol, forms two oily compounds, one, $\text{C}^2\text{H}^4\text{O}^2$, soluble in water, the other, $\text{C}^2\text{H}^4\text{O}^3$, insoluble in water, but soluble in ether; also a white hygroscopic substance, $\text{C}^{12}\text{H}^{20}\text{O}^3$, insoluble in water, alcohol, and ether, probably a condensation-product of ethoxyl-glycide (Laufer, *Jenaische Zeitschrift* [2], iii. 2 Supplementheft, 141).

EPICYANHYDRIN—EPIHYDRINCARBONIC ACID. 735

On the Action of *Hydrocyanic Acid* on Epichlorhydrin, see CYANIDE OF HYDROGEN (p. 610).

EPICYANHYDRIN, $C^3H^3O(CN) = \begin{matrix} OH^2.CN \\ CH \\ OH^2 > O \end{matrix}$. To obtain an abundant yield of

this substance by the action of aqueous potassium cyanide on epichlorhydrin (Paszchke's process, *2nd Suppl.* 466), it is necessary to use potassium cyanide quite free from alkali (recently prepared by fusion of dehydrated potassium ferrocyanide); with the commercial cyanide, or that which is prepared by passing hydrocyanic vapour into alcoholic potash, the yield is very small. Pure epicyanhydrin melts at 168° , and is easily converted by boiling with fuming hydrochloric acid into epihydrin-carbonic acid, $C^3H^3O.CO^2H$ (Hartenstein, *J. pr. Chem.* [2], vii. 295).

EPIDOTE. This mineral occurs in the Allochett-thal, in Tyrol, in crystals accompanied by brown garnet, quartz, Labradorite, and titanite, in clefts of a weathered syenitic rock. The colour of these epidote crystals is blackish-green; some weathered specimens are covered with a crust of ferric oxide, and they occasionally attain a length of 18 mm. Light-coloured, radiating specimens were also found. Ordinary combination $\infty P\infty . P . 0P . P\infty$. Sp. gr. 3.452. An analysis of a fresh crystal gave the following percentage composition:

SiO^2	Al^2O^2	Fe^2O^2	FeO	CaO	H^2O
37.70	24.61	14.23	0.45	20.99	2.23 = 100.21

This analysis agrees tolerably well with the one given by Ludwig of epidote from Salzbach (*2nd Suppl.* 467), also that from Burawa, analysed by Hermann, the amount of lime being however rather lower. This epidote therefore belongs to the lime epidotes, which contain no manganese or magnesia (C. Doelter, *Jahrb. f. Min.* 1876, 67).

Two specimens of manganese epidote from St. Marcel in Piedmont have been analysed by Rammelsberg (*Chem. Centr.* 1873, 576) with the following results:

SiO^2	Al^2O^2	Fe^2O^2	Mn^2O^2	CaO	H^2O
38.29	16.41	8.10	14.72	21.73	1.74 = 100.99
38.64	15.03	8.38	15.00	22.19	1.78 = 101.02

These analyses agree with the ordinary formula of epidote, $Si^2R^2Ca^2H^2O^2$, the symbol R standing for Al, Fe, and Mn. The proportion of these three metals is $Fe : Mn : Al = 1 : 2 : 3$.

On the Optical Properties of the Sulzbach Epidote, see Klein (*Jahrbuch f. Min.* 1874, 1).

On the Corrosion-figures of Epidote, see Baumhauer (*ibid.* 1876, 420).

Epidote (A) from the glaucophane-bearing rocks of the island of Syra has been analysed by Ludecke (*Jahrb. Min.* 1876, 117), and (B) from the diorites of the Ehrenberg near Ilmenau by E. E. Schmid (*ibid.* 56):

	SiO^2	Al^2O^2	Fe^2O^2	Mn^2O^2	CaO	MgO	FeO	H^2O
A.	38.15	25.3	9.3	—	25.1	—	—	1.8 = 99.65
B.	37.8	19.5	15.3	0.2	24.2	0.8	0.3	2.3 = 100.4

The epidote-rock, deposited contemporaneously with the diorites and micaceous gneisses of the Serra Mantiquera in the province of Minas Geraes, Brazil, has been examined by H. Gorceix (*Compt. rend.* lxxii. 688). From measurements of individual crystals by Descloizeaux, it appears that the rock consists mainly of epidote, together with very small quantities of quartz and isolated patches of iron ochre. Sp. gr. after ignition = 3.40:

	Al^2O^2	CaO	FeO	MgO	Loss by ignition
38.5	25.1	23.2	10.4	trace	2.6 = 99.8

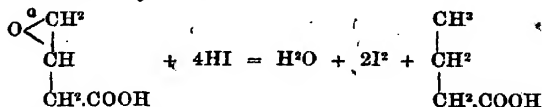
A transformation-product of the hornblende of a hornblende-granite at Kinkigtok in Greenland, nearly related to epidote, and having a sp. gr. = 3.446, is described by Vrbka (*Wien. Akad. Ber.* [1 Abth.], lxxix. 96), and has been analysed by Belohoubek:

SiO^2	Al^2O^2	Fe^2O^2	FeO	CaO	K^2O	Na^2O	H^2O
38.10	10.73	17.57	8.87	21.46	1.03	2.25	0.48 = 100.49

EPIHYDRINCARBONIC ACID, $C^3H^3O^2 = O \begin{matrix} CH^2 \\ | \\ CH \\ | \\ CH^2.CO^2OH \end{matrix}$. This acid, which

Paszchke obtained by the action of acids or alkalis on epicyanhydrin (*2nd Suppl.* 466), is best prepared by boiling epicyanhydrin with fuming hydrochloric acid: it separates on cooling in concentric groups of long needles, and may be purified by recrystallising.

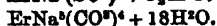
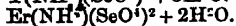
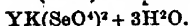
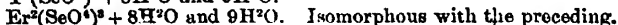
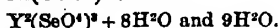
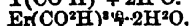
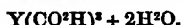
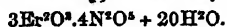
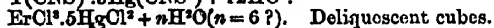
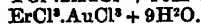
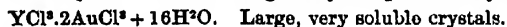
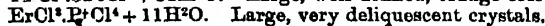
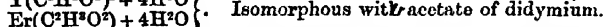
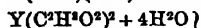
tion from hot water, in which it is easily soluble. It melts at 225° . It does not unite, like epichlorhydrin, with hydrochloric acid, acetyl chloride, or acid sodium sulphite. It is not attacked by tin and hydrochloric acid, or by sodium-amalgam, but when heated for six or seven hours to 160° with fuming hydrochloric acid, it is converted into normal butyric acid:



(Hartenstein, *J. pr. Chem.* [2], vii. 295).

EQUINIC ACID. An acid obtained from fresh mares' milk, in which it appears to exist in combination with ammonia; it crystallises in needles, and exhibits properties different from those of hippuric acid (J. Duval, *Compt. rend.* lxxxii. 419).

ERBIUM and YTTRIUM. Cleve (*Bull. Soc. Chim.* [2], xxi. 344) has continued his investigations of the compounds of these metals, and has come to the conclusion that they are not diatomic as formerly supposed (2nd Suppl. 1311), but triatomic, like the cerite metals. Their atomic weights are accordingly Er = 170.55; Y = 89.55 (according to Rammelsberg E = 169: Y = 92.5). The following salts have been analysed:



A table, compiled by Rammelsberg, of the composition of natural minerals containing the yttrium and cerium metals, according to the old and new atomic weights, is given under CERITE-METALS (p. 419 of this volume).

Spectrum of Erbium.—According to Lecoq de Boisbaudran (*Compt. rend.* lxxvi. 1080), erbium in the pure state—contrary to the observation of Bahr and Bunsen—(*Liebigs Annalen*, cxxvii. 1), gives a spectrum different from that which is produced when the earth is dipped in phosphorus-salt. On directing the central cone of a blowpipe-flame on one surface of the erbium phosphate, so that this part shall be relatively cooler than the rest of the glowing mass, the spectrum is completely reversed. The silicate and borate of erbium likewise exhibit slight diversities in their spectra.

On the Heat of Neutralisation of the Hydroxides of Erbium and Yttrium, see HEAT.

ERGOT. According to Buchheim (*Arch. Pharm.* [3], vii. 32), the substance called *ergotine*, the supposed active principle of ergot (ii. 430; 1st Suppl. 580), is a body closely resembling animal gelatin. It is easily soluble in cold water, and is therefore contained in the cold aqueous infusion of ergot. Like gelatin it gives precipitates with phenylsulphuric acid, tannic acid, and chlorine. It cannot, however, be completely precipitated by tannic acid. It is formed by the action of the mycelium of a fungus on the gluten of rye, by which action the gluten undergoes a series of transformations, terminating in its conversion into leucine, ammonia, and trimethyl-

amine. The decomposition of gluten under the influence of the fungus is, therefore, analogous to the putrefaction of albumin. In both cases albuminous substances undergo a series of transformations different from that which occurs in the healthy animal organism, and the products formed have, in consequence, different properties. The end-products, however, are the same in both series. Ergotine, therefore, belongs to the class of putrid products. See also Squibb (*Amer. Pharm. Assoc. Proc.* 1873, 957; *Pharm. J. Trans.* [3], iv. 912, 956).

The following substances have been obtained from ergot by Dragendorff (*Pharm. J. Trans.* [3], vi. 1001). 1. *Scleromucin*.—This is a nitrogenous colloidal substance extracted from ergot by water, and precipitated by alcohol of 40–45 per cent.: when once dried, however, it dissolves in water with difficulty. It does not give any albuminoid reaction.

2. *Sclerotic acid*.—This body is extracted by alcohol of 45 per cent., and passes into the diffusate in dialysis, but is colloidal after its separation in the pure state. It is precipitated by alcohol of 90 per cent., together with lime, &c., but, after treatment with hydrochloric acid, may be separated from the ash by addition of alcohol. Its solubility in water renders it better adapted than scleromucin for therapeutic purposes. It is tasteless, scentless, slightly hygroscopic, and gives no albuminoid, alkaloid, or glucosidal reactions.

3. *Sclererythrin*.—This compound is contained in the red colouring matter which is dissolved out by alcohol from the residue left on treating ergot with aqueous tartaric acid, and may be separated by further treatment from a brown resinous substance. Sclererythrin is insoluble in water, but soluble in alcohol, ammonia-solution, &c.; its alkaline solutions are of a murexid colour: it forms a red mixture with aluminium sulphate and zinc chloride, and gives a blue precipitate with barium salts, &c. The amount of this body contained in ergot is very small, and it is supposed to stand in near relation to chrysophanic acid and alizarin. Together with sclererythrin another colouring matter is obtained, which when isolated is no longer soluble in water, &c., but dissolves in potash with a violet colour, from which it is precipitated by acetic acid; concentrated sulphuric acid dissolves it with a blue colour, and on this account it has been called *scleroidin*; it is similar to sclererythrin, of which it is probably a decomposition-product.

4. *Sclerocrystallin* and *Scleroxanthin*.—After sclererythrin and scleroidin have been removed from ergot powder, ether takes up a mass which crystallises partly in colourless needle-shaped crystals, partly in lemon-yellow crystals. The needle-shaped crystals (sclerocrystallin) are almost insoluble in water, &c., but soluble in ammonia and potash solutions, and have the composition $C^{10}H^{10}O^4$. The yellow crystalline body (scleroxanthin) appears to be a hydrate of sclerocrystallin, $2C^{10}H^{10}O^4 \cdot 3H^2O$, and is transformed into the latter by heating with chloroform. Neither of these bodies has any effect on frogs.

Dragendorff has also obtained two other substances from ergot, but they have not yet been examined.

A substance called ergotinine, described by Tanret (*Compt. rend.* lxxxi. 896) as an unstable alkaloid existing in very small quantity in ergot, is, according to Dragendorff, a mixture of sclererythrin with other substances. Ecboine (2nd Suppl. 469) he regards as identical with ergotine.

ERIGERON. On the Detection of Adulterations of the Volatile Oil of *Erigeron canadense* with Fixed Oils, see E. J. Week (*Amer. Pharm. Assoc. Proc.* 1872, p. 242).

ERLAN or **ERLANITE**. The supposed mineral species thus designated, from the Erzgebirge (ii. 501), appears, from a microscopic examination by Frenzel (*Jahrb. Min.* 1873, 790), to be a mixture containing quartz, felspar, and garnet.

EUICIC ACID, $C^8H^8O^2$ (ii. 501). G. Goldschmidt (*Wien. Akad. Ber.* lxx. 451) has found this acid, together with benic acid, in the oil expressed from black mustard seed. By the action of hydriodic acid and amorphous phosphorus, it is converted into an acid probably isomeric with benic acid.

ERUPTIVE ROCKS. On the Eruptive Rocks of the Bannat, of Mitylene, and of Styria, see *Jahresbericht f. Chemie*, 1873, 1218–1220. On those of the Fichtelgebirge: *Jahrb. f. Min.* 1874, 435; *Jahresb. f. Chem.* 1874, 1302.

ERYTHRAMYLUM. A substance produced, according to Brücke, by the action of malt-extract on starch (q.v.)

ERYTHRITE, $C^4H^4(OH)^4$. This tetraatomic alcohol, distilled with five times its weight of concentrated formic acid, yields, first, the monoformin of the unsaturated glycol, $C^4H^4(OH)^3$, then carbon dioxide and a hydrocarbon, C^4H^4 (probably ethyl-
3 B

acetylene, C^2H_2 (C^2H^*), which solidifies in a freezing mixture (Henninger, *Bull. Soc. Chim.* [2], **ix.** 2, 145; **xxi.** 242).

On the reaction of erythrite with *dehydrated oxalic acid*, see OXALIC ACID.

ERYTHRODEXTRIN. See DEXTRIN (p. 629).

ERYTHROPHENIC ACID. According to Jacquemin (*Bull. Soc. Chim.* [2], **xx.** 68), the sodium salt of this acid is produced by the action of sodium hypochlorite on a mixture of aniline and phenol. It forms salt-solutions of a deep blue colour, a reaction which may be made available for the detection of aniline or of phenol.

E. guineense, is a tall leguminous tree growing on the west coast of Africa. Its wood is very hard, and is covered with a hard fibrous and odourless bark, which contains an active poison, called erythrophleine. This substance is a base, and may be obtained by extracting the pulverised bark with alcohol, evaporating the tincture to a small bulk, treating this with warm water, evaporating the aqueous extract at a low temperature, rendering it alkaline with ammonia, or sodium carbonate, and extracting with acetic ether. On evaporating the resulting solution, the base is left. It is only slightly soluble in ether, benzene, or chloroform, but dissolves in water, ethyl acetate, amylic alcohol, and ordinary alcohol. It forms salts with acids, and its chloride is precipitated by platinic chloride, forming a double salt. Solutions of erythrophleine exhibit the following reactions:—

Picric acid: yellow green precipitate.

Iodine in potassium iodide: reddish-yellow precipitate.

Iodide of mercury and potassium: white precipitate.

Iodide of bismuth and cadmium: flocculent white precipitate.

Potassium bichromate: yellowish precipitate.

Mercuric chloride: white precipitate.

Auric chloride: whitish precipitate.

Palladium chloride: white precipitate.

In contact with manganese peroxide and sulphuric acid, erythrophleine develops a violet colour, less intense than that produced under similar circumstances by strychnine, and soon changing to a dirty-brown.

Erythrophleine possesses very marked toxic properties, and must be placed amongst those poisons which exert a paralyzing action on the heart; its effects are delayed by curare, but not by atropine (Gallois a. Hardy, *Bull. Soc. Chim.* [2], **xxvi.** 39).

E. Coumunga is a variety resembling *E. guineense*. All parts of it are poisonous, and the poison consists of an alkaloid, the physiological effects of which are similar to those of erythrophleine.

ERYTHROPHYLL. See PLANT-COLOURS.

ERYTHROPYROCATECHIN. See PYROCATECHIN.

ERYTHROXYANTHRAQUINONE. See ANTHRAQUINONE (p. 99).

ESMARKITE. This variety of hydrous dichroite, originally found at Brevig in Finland (ii. 320), occurs also at Vestre Kjørrestad, in Bamle, Norway, forming polysynthetic twins, but as one individual predominates, and innumerable twin laminae are interposed, the crystals appear to be simple. They have a peculiar rounded surface resembling that obtained by fusion, and are often covered with a fine greenish-black crust, which gives them a very peculiar appearance, differing completely from that of felspathic minerals, but approaching that observed on the plagioclases of Bodenmais, Oriskany and Lojo. The crystals exhibited the following forms: ∞P , $\infty P \frac{1}{2}$, $\infty P \frac{3}{4}$, $\infty P \frac{5}{8}$, $0P$, P , $\infty 2P$, $\infty 2P \frac{1}{2}$, P , the types being either tabular through the basal terminal plane, or prismatic. They are twinned according to two laws, *viz.*; (1st) twin-plane the brachypinacoid; (2nd) twin axis, the macrodiagonal. Complete basal cleavage; less complete, parallel to the brachypinacoid. $H=6$. Sp. gr.—2.68. Colour bluish-grey. Pearly lustre on the cleavage planes, resinous lustre on fractures. The esmarkite is accompanied by hornblende, apatite, and magnetic iron pyrites (Brögger a. Reusch, *Jahrb. Min.* 1876, 196).

$C^2H^* = H^*C = CH^*$. This gas, subjected to the action of the silent electric discharge (p. 729), yields free hydrogen, and a small quantity of acetylene, together with resinous hydrocarbons (Berthelot).

On *Nitro-ethanes* see NITRO-PARAFFINS under PARAFFINS.

ETHENE. See ETHYLENE.

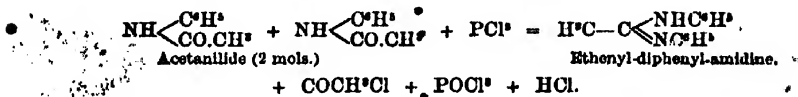
ETHENYL-AMIDOPHENOL, $C^6H^5NO = C^6H^4 \begin{array}{c} \diagup O-C-CH^3 \\ \diagdown N \end{array}$, is formed by

heating ortho-amidophenol with acetic anhydride for some time in a vessel with reflux condenser. It is a colourless liquid, boiling at 200° – 201° , smelling like acetamide, insoluble in water, easily soluble in alcohol, and appears to form a compound with calcium chloride. Sp. gr. = 1.1365 at 0° . It turns reddish when exposed to the air, and, when left for a long time under water, it is converted into acetylamidophenol $C^6H^4(OH)(NH.C^2H^3O)$. The salts of ethenyl-amidophenol are difficult to prepare, on account of the easy decomposition of the base by water. The *sulphate* and *hydrochloride* are crystalline. The *platinohydrochloride*, $(C^6H^4NO.HCl).PtCl_5$, dissolves very easily in dilute alcohol, being apparently resolved at the same time into its components (Ladenburg, *Deut. Chem. Ges. Ber.*, ix. 1624).

ETHENYL-DIETHYL-AMIDINE, or **ETHENYL-DIETHYL-AMINIMIDE**, $C^6H^4N^2 = H^2C - C \begin{smallmatrix} \text{NHC}^2H^5 \\ \text{NC}^2H^5 \end{smallmatrix}$. When acetethylamide $NH(C^2H^5)(C^2H^5O)$

is acted upon by 1 mol. PCl^5 , a brown-red syrup is obtained, which yields a platinohydrochloride, $(C^6H^4ClN^2.HO).PtCl_5$, crystallising in the monoclinic system. The free base, $C^6H^4ClN^2$, separated from this salt, is an oil which has a tarry odour, and cannot be distilled without decomposition. On gently heating it with solid potassium hydroxide, an energetic action takes place, attended with separation of potassium chloride, and lowering of the boiling point of the liquid from 220° to 170° , and ethenyl-diethyl-amidine is formed, as an oily base which boils without decomposition at 165° – 168° , dissolves in water, alcohol, and ether, precipitates most metallic salts, and is capable of dissolving recently precipitated alumina (Wallach a. Hoffmann, *Deut. Chem. Ges. Ber.* iii. 313).

ETHENYL-DIPHENYL-AMIDINE, $C^6H^4N^2 = H^2C - C \begin{smallmatrix} \text{NHC}^6H^5 \\ \text{NC}^6H^5 \end{smallmatrix}$. *Diphenyl-acetdiamine*.—This base, already described as ethenyl-diphenyl-diamine (1st Suppl. 588) was discovered by Hoffmann, who obtained it by the action of phosphorus trichloride on a mixture of aniline with acetanilide or acetyl chloride. E. Lippmann (*Deut. Chem. Ges. Ber.* vii. 641) prepares it by the action of phosphorus pentachloride on acetanilide, and explains its formation by the equation,



When the two bodies, in the proportion indicated, are mixed together in a flask, the mixture becomes hot and liquefies, with evolution of hydrochloric acid; and, on heating the flask with an upright condensing tube attached, the mass turns brown, solidifies, and gives off more hydrochloric acid. The mass is then to be dissolved in water, the base precipitated by ammonia, freed from resin by repeated solution and fractional precipitation with ammonia or potash, and finally purified by crystallisation from alcohol. Wallach a. Hoffmann (*ibid.* viii. 1567) regard ethenyl-diphenyl-amidine as only a secondary product of the decomposition of acetanilide. By treating acetanilide with PCl^5 in such a manner as to avoid rise of temperature, they obtain acetanilide chloride, $CH^3 - CCl = N^2 - C^6H^5$, as a well-crystallised compound, which is strongly acted upon by aniline, with production of ethenyl-diphenyl-amidine. (See ACETANILIDE, p. 8.)

Ethenyl-diphenyl-amidine boiled with dilute alcohol is resolved, by assumption of H^2O , into acetanilide and aniline (p. 71). When treated with *hydrogenising agents* (as Sn and HCl, Zn and HCl, or in acetic acid solution with sodium-amalgam), it does not, as might be expected, take up H^2 and yield ethylidene-diphenyl-diamine, $H^2C - CH(NH.C^6H^5)_2$, but is resolved, by assumption of $2H^2O$, into acetic acid and 2 mol. aniline. With *bromine*, it forms a dibromide which crystallises with difficulty in broad laminae. With *fuming nitric acid*, it yields the nitrate of ethenyl-dinitrophenyl-amidine, $C^6H^4(NO^2)_2N^2.NO^2H$, which does not dissolve in water, alcohol, ether, alkalis, or acids, but is gradually converted by boiling with water or acids in sealed tubes, into nitroaniline (m. p. 141°), and by reduction into paraphenylenediamine (Lippmann).

ETHENYL-PHENYLENEDIAMINE, $OH^2N^2 = C^6H^5 - C \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} - C^6H^5$, is obtained by boiling orthophenylenediamine with glacial acetic acid (Ladenburg, *Deut. Chem. Ges. Ber.* viii. 677), or by reduction of orthonitracetanilide with tin and glacial acetic acid (Hübner a. Rudolph, *ibid.* 471). It crystallises in long shining needles which melt at 170° (Hübner a. Rudolph), at 175° (Ladenburg), deliquesce in ether, and dissolve easily in alcohol and water. The *hydrochloride* and *sulphate* form easily

soluble needles; the *platino-chloride* is very efflorescent; the *nitrate* is less soluble, and forms thick shining yellowish needles (Hübner a. Rudolph).

Acetoluidide, treated with phosphorus pentachloride, is converted into acetoluidide imidochloride, $\text{H}^*\text{C}-\text{C}\begin{smallmatrix} \text{Cl} \\ \text{NC}^*\text{H}^* \end{smallmatrix}$, which, when treated with aniline, toluidine, or naphthylamine, yields:

Ethenyl-phenyl-tolylamidine, $\text{H}^*\text{C}-\text{C}\begin{smallmatrix} \text{NHC}^*\text{H}^* \\ \text{NC}^*\text{H}^* \end{smallmatrix}$, in white needles, melting at $86^\circ-88^\circ$.

Ethenyl-ditolylamidine, $\text{H}^*\text{C}-\text{C}\begin{smallmatrix} \text{NHC}^*\text{H}^* \\ \text{NC}^*\text{H}^* \end{smallmatrix}$, m. p. $117^\circ-118^\circ$.

Ethenyl-naphthyl-tolylamidine, $\text{H}^*\text{C}-\text{C}\begin{smallmatrix} \text{NHC}^*\text{H}^* \\ \text{NC}^*\text{H}^* \end{smallmatrix}$.

The imidochloride is converted by heat into the hydrochloride of a base, $\text{C}^*\text{H}^*\text{CIN}^*$, which melts at $71^\circ-72^\circ$, and decomposes at about 130° , turning brown, and yielding the hydrochloride of a new base (Fassbender, *Deut. Chem. Ges. Ber.* ix. 1214).

ETHENYL-TOLYLENE-DIAMINE, $\text{C}^*\text{H}^*\text{C}\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}\text{C}^*\text{H}^*$, is formed by boiling parameta-tolylene-diamine (m. p. 89°) with glacial acetic acid. It melts at $196^\circ-198^\circ$, and is converted by fuming nitric acid into a nitro-derivative, which crystallises in needles, and decomposes without fusion at $183^\circ-185^\circ$ (Ladenburg, *ibid.* viii. 677).

ETHENYL-TRICARBONIC ACID, $\text{C}^*\text{H}^*\text{O}^*=\text{H}^*\text{O}^*-\text{C}(\text{CO}^*\text{H})^*$, is formed from ethylic monobromosuccinate by successive treatment with potassium cyanide, hydrochloric acid, and alcoholic potash (Orlowski, *Deut. Chem. Ges. Ber.* ix. 1604).

Formation.—A mathematical theory of the laws of etherification, experimentally established by Berthelot a. Péan de St.-Gilles (1st Suppl. 586), as given by J. H. van 't Hoff (*Deut. Chem. Ges. Ber.* x. 669; *abstr. Chem. Soc. J.* 1877, ii. 679). The formula which expresses the amount of etherification produced is exactly similar to that which J. Thomsen has deduced for the partial decomposition of salts by acids (*Pogg. Ann.* cxxxviii. 65), the two formulae, moreover, containing the same constants. Hence it appears that the formation of ethers, and the partial decomposition of salts by acids, follow the same laws.

Experiments on the etherification of various alcohols by *acetic acid* have been made by N. Menschutkin (*Deut. Chem. Ges. Ber.* x. 1728). The experiments consisted in heating glass tubes of about 1 c.c. capacity, containing mixtures of alcohol and acetic acid in molecular proportions, in a bath of glycerin heated to $153^\circ-154^\circ$. The amount of ether thus formed in a given time was estimated by withdrawing a tube from the bath, cooling it quickly, and determining the residual acetic acid by titration with baryta-water.

In this way an estimate was obtained of the amount of ether formed in 1, 2, 4, 7, 10, 14, 24, 36, 42, 48, 72, 96, 120, and in a few cases 144 and 168 hours. The most important data are—(1). The initial rates of etherification (that is, the proportion of ether formed in the first hour, expressed in percentage of the total theoretical amount), and (2), the limit of etherification, similarly expressed. These numbers are given in the following table:

	Initial rate	Limit
Methyl acetate	57.25	71.45
Ethyl "	46.60	69.61
Propyl "	46.39	70.90
Isobutyl "	45.40	73.46
Octyl "	46.56	82.24
Cetyl "	—	87.17
Allyl "	36.80	61.88
Benzyl "	37.77	63.97
Styryl "	37.21	64.58

A distinction has to be made between the absolute and the relative rate of etherification, meaning by the former the proportion of alcohol or acid actually etherified to the total quantity employed, and by the latter the proportion of ether formed, to the amount determined by the limit of etherification. As regards the primary saturated alcohols, it is found that methyl alcohol differs considerably in its initial rate (absolute, 57.25; relative, 80.1) from the rest, which all have an absolute initial rate of about 46.5. A review of the whole of the numbers furnished by these alcohols (with the exception of methyl) shows that, though the rate of etherification during the first hour is nearly the same in all, it afterwards becomes distinctly

greater in alcohols of higher molecular weight: hence the limit is also higher, as is shown by the table.

The relative rate of etherification decreases regularly with increase of molecular weight, the numbers for ethyl, propyl, isobutyl, and octyl alcohols being respectively 67.94, 65.43, 61.80, and 56.64.

In the non-saturated alcohols the initial rates, which are nearly the same in all, are about 10 lower than in the saturated alcohols. The relative rates for allyl, benzyl, and styryl alcohols are 59.46, 59.04, and 57.61 respectively.

The limit of etherification of the saturated primary alcohols (omitting methyl alcohol) increases with the molecular weight, being about two greater for each higher homologue, as is shown by the foregoing table. This seems to show that differences in molecular weight have a much greater influence upon the limit of etherification than was thought by Berthelot and Péan de St.-Gilles.

Formation from Nitrils.—Ethers are readily formed by the action of hydrochloric or sulphuric acid on solutions of the nitrils in absolute alcohol, e.g. ethyl acetate from acetonitril, ethyl propionate from propionitril, and ethyl benzoate from benzonitril (Beckurts a. Otto, *Chem. Centr.* 1877, p. 5).

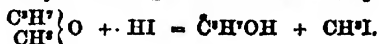
Cohesion.—By determination of the weight required to separate a circular plate from the surface of various liquids, and by observation of the heights to which the liquids rise in capillary tubes, it is found that, of all liquids yet examined, the compound ethers are the least cohesive, and amongst these, the cohesive force is smallest in the sulphur-ethers (R. Schulz, *Pogg. Ann.* cxlviii. 62-76).

Action of Hydriodic Acid on Ethers.—Simple ethers treated with this acid at low temperatures (0° to 4°), are converted into alcohols and the corresponding iodides, e.g.:



Methyl oxide, however, yields only methyl iodide without the alcohol.

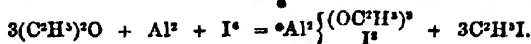
Mixed ethers are acted on in a similar manner, the iodine attaching itself to the lower, and the hydroxyl to the higher alcohol-radicle; e.g.:



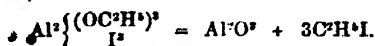
With mixed ethers containing methyl, the reaction is so complete that it may be used as a means of preparing alcohols not easily obtainable by other means. The corresponding hydrocarbon, C^2H^{2n+2} , is to be converted into the chloride, and the chloride into the mixed ether, $C^2H^{2n+1}-O-CH^3$, which, when treated with hydriodic acid gas, will give the alcohol, $C^2H^{2n+1}OH$ (Silva, *Compt. rend.* lxxxi. 323).

Action of Iodine and Aluminium.—Ethyl oxide is not affected by boiling with aluminium and aluminic iodide, but, on bringing it in contact with iodine and aluminium, a brisk action takes place for a few minutes; and if the flask be then heated by immersion in boiling water, a brownish ethereal liquid distils over, and a brown semi-solid substance remains in the flask, which, when heated to 150° , and afterwards to 200° , gives off more of the oily liquid, and leaves a light brown residue almost wholly soluble in water and in alcohol. This residue, heated over a lamp, gives off gas partly absorbable by bromine—the remainder burning with a faintly luminous flame—and leaves a residue of alumina mixed with a little iodine.

The oily liquid, after being washed with water, consists mainly of ethyl iodide, and the soluble residue of aluminic iodethylate, formed according to the equation,

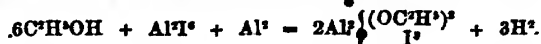


The quantity of ethyl iodide obtained is however greater than that which agrees with this equation, so that the iodethylate probably suffers partial decomposition into alumina and ethyl iodide, thus:



At higher temperatures the ethyl iodide is likewise decomposed, yielding the gaseous products above mentioned.

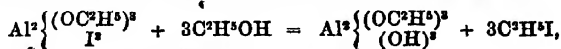
Aluminium iodethylate is also formed, with evolution of hydrogen, when ethyl alcohol is heated to 100° with aluminium and its iodide:



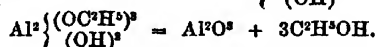
The residue in the flask consists of aluminic iodethylate mixed or combined with alcohol, and when heated to 100° to 200° gives off alcohol and ethyl iodide, leaving

742 ETHIONIC ACID—ETHOXYPARAMIDOBENZOIC ACID.

alumina with a small quantity of iodine. The ultimate result is therefore the same as that in the experiment with ether, but the decomposition of the iodethylate into alumina and ethyl iodide appears to be facilitated by the alcohol contained in the residue, in fact, by addition of alcohol in successive quantities, the whole of the iodine may be ultimately converted into ethyl iodide. The reaction may therefore be supposed to take place in two stages, as represented by the equations,

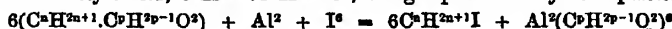


and



Amyloxyde, $(\text{C}^5\text{H}^{11})^2\text{O}$, is acted upon by iodine and aluminium in the same manner as ethyl oxide, yielding amyl iodide and aluminic iodamylate, $\text{Al}^3(\text{OC}^5\text{H}^{11})^3\text{I}^3$.

The acetates of ethyl and amyl also suffer a similar decomposition, yielding iodide of ethyl or amyl, and acetate of aluminium, the action in the case of any compound of the fatty series, $\text{C}^n\text{H}^{2n+1}.\text{C}^n\text{H}^{2n-1}\text{O}^2$, being represented by the equation,



(Gladstone & Tribe, *Chem. Soc. J.* 1876, ii. 357).

On the Relation between the Boiling Points of Compound Ethers and their Molecular Structure, see BOILING POINTS under HEAT.

On the Efflux-coefficients of Ethers, see LIQUIDS.

On the Heat of Formation of Ethers, see HEAT.

On Titanic Ethers, and the Compounds of Ethers with Titanium Tetrachloride, see TITANIUM COMPOUNDS.

ETHIONIC ACID, $\text{C}^2\text{H}^4\text{S}\text{O}^2 = \text{C}^2\text{H}^4 \begin{array}{c} \text{O.SO}^2.\text{OH} \\ \text{SO}^2.\text{OH} \end{array}$. This acid is most easily prepared by the direct action of sulphuric acid on isethionic acid, $\text{C}^2\text{H}^4(\text{OH})(\text{SO}^2\text{H})$. Barium isethionate is triturated with the calculated quantity of sulphuric acid, the mixture diluted with water and filtered, and the filtrate saturated with barium carbonate. The solution, after another filtration, is evaporated on the water-bath, the residue stirred up with water, the separated barium sulphate filtered off, the filtrate again evaporated, and these operations are repeated as long as barium sulphate continues to separate. By this treatment about $\frac{2}{3}$ of the isethionic acid is found to be converted into ethionic acid (Erlenmeyer & Carl, *N. Rep. Pharm.* xxiii. 428).

ETHOMETHOXYBENZOIC or **METHYL-ETHYL-PROTOCATECHUIC ACID**, $\text{C}^8\text{H}^7(\text{OCH}^3)(\text{OC}^2\text{H}^5)\text{CO}^2\text{H}$. See BENZOIC ACIDS (DIOXY-), (p. 291).

ETHOKALIC ACID. The potassium salt of this acid, $\text{C}^2\text{O}^4(\text{C}^2\text{H}^3)\text{K}$, heated to $210^\circ\text{--}215^\circ$, gives off carbon monoxide, and is converted into ethyl-carbonate, $\text{CO}^2(\text{C}^2\text{H}^3)\text{K}$ (Eltzoff, *Deut. Chem. Ges. Ber.* vi. 1259).

ETHOXYDRACYLIC or **ETHYL-PARAOXYBENZOIC ACID**, $\text{C}^8\text{H}^7(\text{OC}^2\text{H}^5)\text{—CO}^2\text{H}$, is formed by oxidising ethyl phloretic acid, $\text{C}^8\text{H}^7(\text{OC}^2\text{H}^5)\text{—CO}^2\text{H}$, with cold chromic acid mixture. As thus produced it melts at 195° , and exhibits all the other properties ascribed to it by Ladenburg & Fittz (1st. *Suppl.* 898). See PHLORETIC ACID (Körner & Corbetta, *Deut. Chem. Ges. Ber.* vii. 1731).

ETHOXYISOBUTYRIC ACID, $\text{H}^3\text{C} \begin{array}{c} \text{H}^3\text{C} \\ \text{H}^3\text{C} \end{array} \text{C} \begin{array}{c} \text{OC}^2\text{H}^5 \\ \text{COOH} \end{array}$ is formed, as potassium salt, by the action of alcoholic potash on an alcoholic solution of monobromoisobutyric acid. It is a colourless liquid, of penetrating ethereal odour, and pungent burning taste, soluble in alcohol and ether, and sparingly in water. Sp. gr. at $0^\circ = 1.0211$; at $16^\circ = 1.0101$, water at the same temperatures being 1. It forms easily soluble and crystallisable salts. The silver salt, $\text{C}^4\text{H}^{11}\text{O}^2\text{Ag}$, crystallises from hot water in white laminae, which in the moist state quickly turn brown in the light. The lead salt, $(\text{C}^4\text{H}^{11}\text{O}^2)_2\text{Pb} + \text{H}^2\text{O}$, crystallises from water, in white translucent prisms. The barium salt, $(\text{C}^4\text{H}^{11}\text{O}^2)_2\text{Ba} + \text{H}^2\text{O}$, forms thick transparent prisms. The zinc salt, $(\text{C}^4\text{H}^{11}\text{O}^2)_2\text{Zn}$, when freshly prepared, crystallises from hot water in pearly laminae, which gradually lose water when dried by heat or over sulphuric acid, and yield an insoluble basic salt. The copper salt forms green laminae; the sodium salt a granular crystalline mass; both easily soluble in water and alcohol (Hell & Waldbauer, *Deut. Chem. Ges. Ber.* x. 448).

ETHOXYPARAMIDOBENZOIC ACID, $\text{C}^8\text{H}^{11}\text{NO}^2 = \text{C}^8\text{H}^7(\text{OH})\text{—C}^2\text{H}^3(\text{NH}^2)\text{COOH}$ (Ladenburg, *Deut. Chem. Ges. Ber.* vi. 129). This acid, metameric with tyrosine, $\text{C}^8\text{H}^7(\text{OH})\text{—C}^2\text{H}^3(\text{NH}^2)\text{COOH}$ (paraphenoxy-amidopropionic acid, 1st *Suppl.* 1113), is prepared by heating ethylene oxide and paramidobenzoic

acid (1 mol. of each) in sealed tubes to 50° for two days, rinsing out the contents of the tubes with cold water, which dissolves but very little of them, then repeatedly washing the residue with cold alcohol, and crystallising it several times from warm very dilute alcohol.

Ethoxyparamidobenzoic acid thus obtained crystallises in beautiful prisms, sparingly soluble in cold water and alcohol, easily in hot dilute alcohol. It melts at 187°. Its solutions give no turbidity with lead acetate, whereas this salt added to hot solutions of paramidobenzoic acid, produces after a few seconds a crystalline precipitate consisting of a double salt of paramidbenzoate and acetate of lead, $\text{C}^2\text{H}^3\text{NO}^2 > \text{Pb}$.

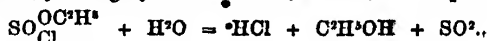
Ethoxyparamidobenzoic acid unites both with acids and with bases. The metallic ethoxyparamidobenzoates are for the most part easily soluble in water. Ethoxyparamidobenzoic nitrate, $\text{C}^2\text{H}^3\text{NO}^3 \cdot \text{HNO}^3$, is formed by dissolving the acid in very dilute nitric acid, and separates on leaving the solution to cool, in laminae, the solution of which when slowly evaporated yields the salt in beautiful needles and prisms.

ETHOXYTHIONYL CHLORIDE, $\text{SO}(\text{OC}^2\text{H}^3)\text{Cl}$, is formed by the action of phosphorus pentachloride on the ethylic sulphite prepared from sulphur chloride and alcohol:



The action takes place at ordinary temperatures, merely requiring the aid of heat towards the end. The same compound is formed, though in small quantity only, by passing hydrochloric acid gas into alcohol saturated with sulphurous acid, and heating the resulting liquid in a sealed tube placed in the water-bath.

• Ethoxythionyl chloride is a colourless, slightly fuming liquid, which boils at 122°; the isomeric compound ethyl-sulphonic chloride, $\text{SO} \begin{smallmatrix} \text{OC}^2\text{H}^3 \\ \text{C}^2\text{H}_5 \end{smallmatrix}$, boils at 171°. It is readily decomposed by water, yielding hydrochloric acid, alcohol, and sulphurous oxide:



It is not attacked by phosphorus pentachloride at the temperature of the boiling liquid, but when heated therewith in sealed tubes to 180°, it yields phosphorus oxychloride and thionyl chloride:



Since thionyl chloride and alcohol yield ethylic sulphite (v. 554), and the preceding experiments show that the two ethyl-groups in this ether can be successively replaced by chlorine, it follows that ethylic sulphite has the symmetrical constitution, $\text{SO} \begin{smallmatrix} \text{OC}^2\text{H}^3 \\ \text{OC}^2\text{H}^3 \end{smallmatrix}$ (Michaelis & Wagner, *Deut. Chem. Ges. Ber.* vii. 1073).

ETHYL ALCOHOL. This alcohol, and some of its compound ethers (acetic, butyric, &c.), have been detected, together with methyl alcohol, in several growing plants, namely in the fruit and umbel-stalks of *Heracleum giganteum*, the fruit of the parsnep (*Pastinaca sativa*), and the unripe fruit of *Anthriscus cerefolium*, and must therefore be regarded as an occasional constituent of plant-juices which have not undergone the process of fermentation (Gutzeit, *Liebig's Annalen*, clxxvii. 344; *Chem. Soc. J.* 1875, p. 1247).

Ethyl alcohol is produced in the fermentation of dough, and though the greater part evaporates during baking, a small quantity remains in the bread, amounting, according to Bolas (*Chem. News*, xxvii. 271), to 0.314 per cent. Slices of bread which had been kept for a week in a moderately warm room, were still found to contain from 0.12 to 0.132 per cent. alcohol.

Ethyl alcohol sometimes occurs in considerable quantity in crude wood-spirit. A sample of this spirit from Kahlbaum's factory in Berlin, was found by V. Hemilian to yield, as principal fraction, a liquid boiling between 78° and 80°, one-fourth of which consisted of ethyl alcohol (*Deut. Chem. Ges. Ber.* viii. 661).

Markownikoff (*ibid.* ix. 1441, 1603) has detected alcohol and acetone in the urine of diabetic patients, and supposes that both these substances are formed in the organism by a fermentation of glucose induced by a peculiar acetone ferment.

Formation.—1. From Ethylene. This gas, brought in contact with strong sulphuric acid in Butlerow's apparatus for effecting the continuous absorption of gases by liquids (*Deut. Chem. Ges. Ber.* iii. 422), is not absorbed at ordinary temperatures; but on heating the apparatus to 160°–175° (in vapour of turpentine oil), rapid and continuous absorption takes place; and on subsequently distilling the liquid with

water, and treating the distillate with potash, considerable quantities of alcohol are obtained. In Berthelot's method of effecting the absorption of ethylene-gas with sulphuric acid by continued agitation (i. 72), it is not improbable that the effect was due to the heat developed by the agitation (Gorai now a. Butlerow, *Liebigs Annalen*, clxix. 146).

2. From milk-sugar. According to Reichardt (*Arch. Pharm.* [3], v. 210), milk-sugar in contact with yeast passes into alcoholic fermentation at 30°. This observation explains the preparation of an alcoholic drink, namely koumiss, from mares' milk, in the warm climate of Asia, also the prevention of fermentation in milk by rapid cooling and preservation in cool places, and protection from the contact of ferments such as dough, yeast, water containing fermenting liquids, &c.

Preparation of Absolute Alcohol.—According to C. Bullock (*Pharm. J. Trans.* [3], iv. 891), the distillation of spirit over quick-lime yields but a small quantity of perfectly absolute alcohol, the first and last portions of the distillate always containing water. All the distillates contain lime, which may be removed by distillation over tartaric acid. J. L. Smith (*Amer. Chemist*, v. 120) prepares absolute alcohol by shaking 180 grams of coarsely pounded quick-lime into 1½ litre of alcohol of 94 per cent., and leaving the mixture to itself for a week, whereby the alcohol is brought up to the strength of 98 per cent. This stronger alcohol is then drawn off by a siphon, heated for two hours in a vessel with reversed condenser with a fresh quantity of lime (120 grams to a litre) and then distilled.

According to Dittmar a. Stewart (*Chem. News*, xxxiii. 53), the last portions of water are retained by alcohol with great obstinacy. Alcohol containing from 5 to 28 per cent. water boils between 77.4° and 78° (absolute alcohol at 78°).

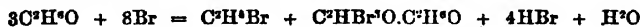
Oxidation by Ozone.—According to A. Boillot (*Compt. rend.* lxxvi. 1132), absolute alcohol through which ozonised oxygen or air is passed, yields acetic acid, formic acid, and apparently also ethyl acetate. There is also formed a very small quantity of a compound which remains, on evaporation of the alcohol, as a white powder soluble in water.

By Electrolytic Oxygen.—When ethyl alcohol, slightly acidulated with dilute sulphuric acid, is submitted to electrolysis, hydrogen gas is evolved at the negative pole, but the oxygen, which would otherwise be liberated, is entirely consumed in oxidising the alcohol. In experiments made by A. Renard (*Compt. rend.* lxxx. 105), the liquid distilled after 48 hours' action began to boil at 42°, the boiling point rising gradually to 80°, and the distillate saturated with calcium chloride, and fractionated, yielded a considerable quantity of aldehyde, ethyl formate, and ethyl acetate, together with very small quantities of acetal, $C^2H^4 \begin{cases} OC^2H^3 \\ OC^2H^3 \end{cases}$ and ethylidene

monethylate, $C^2H^4 \begin{cases} OC^2H^3 \\ OH \end{cases}$. This last compound, which passes over between 80° and 90°, is not attacked by alkalis, but is oxidised by chromic acid to acetic acid, the molecular weight, represented by the formula just given, yielding sensibly 2 mols. of that acid. The residue of the distillation of the oxidised alcohol contained ethyl-sulphuric acid, likewise resulting from the electrolytic action.

Action of Platinum-metals.—Finely divided rhodium, iridium, and ruthenium in presence of an alkali, decompose alcohol, with elimination of hydrogen and formation of an acetate (Deville a. Debray, *Compt. rend.* lxxviii. 1782).

Action of Bromine.—When bromine is dropped at intervals, so as to avoid rise of temperature, into absolute alcohol contained in a long-necked flask, the neck then sealed, and the flask heated on the water-bath for several hours till the liquid has become colourless, gas escapes on opening the flask, and the liquid is found to be separated into two layers, the upper consisting of aqueous hydrobromic acid, and the lower of ethyl bromide, free bromal, and bromal alcoholate, $C^2HBr^2O.C^2H^3O$ or $CBBr^2.CH_2(OH)(OC^2H^3)$. The reaction may be represented by the equation,



(E. Hardy, *Compt. rend.* lxxix. 806).

Detection and Estimation.—Riche a. Bary (*Compt. rend.* lxxxii. 768) employ, for the detection of ethyl alcohol in presence of methyl alcohol, acetone, formic acid, and other substances, the violet coloration which acetaldehyde, in common with some other bodies of the same class, produces with solutions of rosaniline.

About 4 c.c. of the liquid to be examined are placed in a flask with 6 c.c. of ordinary sulphuric acid and 10 c.c. of water; 7 or 8 c.c. are then distilled over into 10 c.c. of water; and to this liquid 5 c.c. of sulphuric acid, together with 10 c.c. of solution of permanganate of 4° B., are subsequently added. After five minutes have elapsed

4 c.c. of solution of sodium thiosulphate of 33° B. and 4 c.c. of solution of magenta (.02 grm. per litre) are added. Under these conditions wood-spirit unmixed with ethyl alcohol gives a yellowish-white liquid; but if ethyl alcohol is present the solution assumes a violet colour, the intensity of which necessarily varies with the quantity of aldehyde formed.

Acetone, formic acid, and isopropyl alcohol, treated in a similar manner, give no coloration; moreover, while normal propyl-, isobutyl-, and isoamyl-alcohols are not found in commercial wood-spirit, their aldehydes under similar circumstances affect rosaniline in a manner totally different from that of common aldehyde, and do not produce a violet coloration.

The presence of alcohol may also be detected in water by means of this reaction; the sensibility of the test being sufficient to detect 1 part of alcohol in 1,000 parts of water.

For the detection and estimation of ethyl-alcohol in wood-spirit, Berthelot heats the liquid with twice its volume of strong sulphuric acid. If only 1 per cent. of ethyl-alcohol is present, ethylene gas is evolved and may be estimated with bromine (*Compt. rend.* lxxx. 1039).

For the detection of fusel oil in alcohol, Böttger recommends the use of a dilute solution of potassium permanganate, which is decolorised by amyl alcohol much more easily than by ethyl alcohol (*Dingl. pol. J.* ccvii. 516). The method recommended by Bouvier (*Zeitschr. anal. Chem.* 1872, 343), consisting in shaking up the spirit with a few lumps of potassium iodide, whereby a light yellow colour is said to be imparted to the liquid in consequence of the separation of iodine, is, according to Böttger, not to be relied on, inasmuch as potassium iodide is not decomposed by pure amyl alcohol, but only by the acids which are present in spirit of inferior quality.

For the estimation of ethyl alcohol in tinctures, Rosenblatt (*Russ. Zeitschr. Pharm.* 1872, 518) introduces into a burette holding 16 cub. cent. divided into 6.1 cub. cent. and closed at the bottom, 7 cub. cent. of official chloroform, and 8 cub. cent. of the alcoholic liquid under examination; then closes the burette with a cork; shakes the liquid vigorously; places the burette for a few minutes in water of 40°–60°; agitates again; and cools the liquid to 17°. The volume of the two liquids should then measure exactly 15 cub. cent.; if it is larger the agitation must be repeated. An exact observation is now to be made of the division of the burette which coincides with the surface of separation of the two liquids, and the amount of alcohol is calculated from the following table:

Cub. cent.	Alcohol.*
2.5	gives 75 per cent. Tralles.
2.7	" 73 "
2.9	" 71 "
3.0	" 70 "
3.2	" 68 "
3.45	" 66 "
3.75	" 64 "
4.05	" 62 "
4.4	" 60 "

A comparison of different methods of estimating alcohol, viz. by the vaporimetric method, the distillation method, and the saccharimetric method, is given by A. Kraft (*Zeitschr. anal. Chem.* 1873, 48; *Jahresb. f. Chem.* 1873, 951).

On a Compound of Ethyl-alcohol with Allyl cyanide, $C^3H^3CN.3C^2H^5O$, see 2nd Suppl. p. 491; with Antimonic Chloride, see ANTIMONY (p. 114).

ETHYL BROMIDE, BROMINATED. Ethyl bromide treated with bromine yields bromethyl bromide or ethylidene bromide, $CH^2=CHBr^2$ (b. p. 114°), ethylene bromide, $CH^2Br_2=CH^2Br^2$ (b. p. 131°), and dibromethyl bromide, $C^2H^2Br^2=C^2H^2Br^2$ (b. p. 137°). The first two compounds may be completely separated from one another by an alcoholic solution of potassium hydrosulphide, the bromethyl bromide remaining unaltered whilst the ethylene bromide is converted into ethylene-mercaptan, $CH^2(SH)=CH^2(SH)$.

When bromethyl bromide thus purified is treated with aqueous or alcoholic ammonia, it yields collidine, $C^8H^{11}N$, boiling at 181°. With potassium acetate in alcoholic solution, it yields aldehyde and acetal; but ethylene diacetate, which Caventor mentions as one of the products (*1st Suppl.* 594), was not observed by Tawildarow. Bromethyl bromide, heated with water and lead oxide, yields nothing but aldehyde.

Dibromethyl bromide, $CH^2Br=CHBr^2$, is also produced by the action of bromine on ethylene bromide. Treated with sodium ethylate it forms two isomeric compounds, $C^2H^2Br^2$, one of which boils at 91°, the other at 168°.

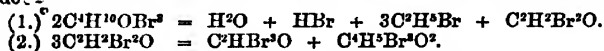
C^2H^3Cl Action of Sulphuric Anhydride.—The

secondary products formed in this reaction, and occurring in the wash-waters obtained on treating the chlorosulphuric ether, $C^2H^5O.SO^2.Cl$, which is the chief product, with water, have been examined by E. v. Purgold (*Deut. Chem. Ges. Ber.* vi. 502). On separating the free sulphuric and ethylsulphuric acid by boiling with lead carbonate, freeing the filtrate from lead by sulphuretted hydrogen, evaporating off the free hydrochloric acid, and neutralising the solution with barium carbonate, a chlorinated barium salt was obtained, the quantities of chlorine and barium in which corresponded with mixture of barium isethionate and chlorisethionate. On adding alcohol to the liquid and leaving it to itself for a while, the chlorisethionate, $(C^2H^4ClSO^2)^2Ba + 2H^2O$, crystallised out in the pure state. The presence of isethionic acid was not directly proved, but its supposed existence in the mixture is corroborated by the fact that this acid is formed, with evolution of hydrochloric acid, by the action of fuming sulphuric acid on ethylsulphuric chloride, $C^2H^5O.SO^2.Cl$, a reaction analogous to the conversion of ethylsulphuric into isethionic acid by the action of sulphuric anhydride, observed by Meves (*Liebig's Annalen*, cxliii. 64), and to the formation of oxethylene-disulphonic acid by the action of sulphuric anhydride in excess on ethyl chloride, observed by Purgold. From these results it may be inferred that the action of sulphuric anhydride on ethyl chloride gives rise to the formation of the three isomeric compounds, chlorisethionic acid, $C^2H^4Cl.SO^2.OH$, isethionic chloride, $C^2H^4(OH).SO^2.Cl$, and ethylsulphuric chloride, $C^2H^5O.SO^2.Cl$ (v. Purgold, *Deut. Chem. Ges. Ber.* vi. 502).

ETHYL IODIDE, $C^2H^5.I$. It has been observed by Paternò (*Gazz. chim. ital.* iv. 149), and confirmed by H. Schiff (*Deut. Chem. Ges. Ber.* vii. 592), that in the preparation of this ether (and of ethyl acetate) a better product is obtained with hydrated than with absolute alcohol.

ETHYL OXIDE, $(C^2H^5)^2O$. *Action of Ozone*.—When a slow stream of ozone (produced from oxygen by a succession of electric discharges, and carefully dried with sulphuric acid) is passed into ether, each bubble produces a violent reaction, and a liquid gradually settles to the bottom, consisting chiefly of acetic and oxalic, with a little formic acid, a larger quantity of hydrogen dioxide, and probably also small quantities of aldehyde (A. W. Wright, *Sil. Am. J.* [3], vii. 184).

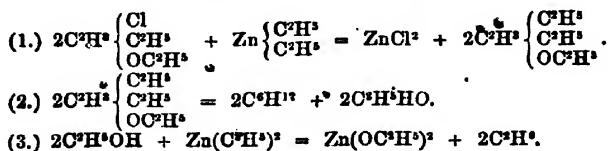
Compound with Bromine, $2C^2H^5O.3Br^2$.—This compound is formed, by direct combination of ether and bromine, as a heavy garnet-red oil which solidifies in a freezing mixture. When purified by draining off the liquid portion and recrystallising, it consists of brilliant plates resembling chromic trioxide and melting at about 22° . It has a strong and irritating odour, but does not give off bromine at the ordinary temperature; it is very deliquescent, and is decomposed by water into its constituents. On keeping it for some time, it becomes liquid and gives off hydrobromic acid. When it is heated, ebullition begins at 80° , and hydrobromic acid and ethyl bromide are produced. By heating it in a water-bath in sealed tubes, it is resolved into water, hydrobromic acid, ethyl bromide, dibromaldehyde, bromal and tribromodialdehyde:—



Tribromodialdehyde, $C^2H^4Br^2O^2$, is a colourless, heavy, oily liquid, boiling at about 176° , and having a strong and penetrating odour (Schützenberger, *Compt. rend.* lxxv. 1511).

On the Compound of Ethyl Oxide with *Antimonic chloride*, see ANTIMONY (p. 114).

Diethyl Ethyl Oxide, $C^2H^5O.C^2H^5.O.C^2H^5(C^2H^5)^2$ (Lieben, *Liebig's Annalen*, clxxviii. 1). This compound is most conveniently prepared by digesting chlorethyl ethyl oxide, $C^2H^5O.C^2H^5(C^2H^5.Cl)$, with rather less than the theoretical quantity of zinc-ethyl in a copper vessel in which a pressure of about one extra atmosphere is maintained. Among the products are alcohol, hexylene, zinc ethylate, and ethane. The reactions may be represented as follows:—



Besides the above mentioned substances, two viscous products were obtained, one of which boiled at about 200° , while the other boiled above 300° . The former of

these gave numbers corresponding with the formula $C^2H^4O^2$, and was probably formed by the elimination of $2HCl$ from 2 mols. of chlorethyl ethyl oxide; while the latter, which contained C^2H^4O , was perhaps derived from 5 mols. of chlorethyl ethyl oxide, with elimination of $5HCl$ and $4C^2H^4O$.

The crude diethyl ethyl oxide, obtained as above described, boiled at 125° – 150° , and contained about 6 per cent. of chlorine, this being clearly due to the presence of unaltered chlorethyl ethyl oxide; and prolonged digestion with zinc-ethyl, or with sodium and ethyl iodide, did not entirely convert this compound into diethyl ethyl oxide, while its separation by fractional distillation was found to be impracticable. The last traces of chlorethyl ethyl oxide were, however, removed by the long continued action of metallic sodium at 140° , and then fractionation yielded pure diethyl ethyl oxide. The sodium employed in the above process becomes converted into a yellowish product, which contains sodium ethylate and the sodium salt of some organic acid or acids. Diethyl ethyl oxide may also be prepared by the action of zinc on a mixture of chlorethyl ethyl oxide and ethyl iodide.

Diethyl ethyl oxide boils at 131° , and has a sp. gr. of 0.7865 at 0° , 0.7702 at 20° , and 0.7574 at 40° . Heated to 120° – 140° for 20–30 hours with hydriodic acid of sp. gr. 1.95, it is converted into ethyl iodide and hexyl iodide:

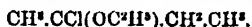


and the hexyl iodide treated with silver acetate and glacial acetic acid, yields a hexylene boiling at 67° – 68° , and a hexyl acetate boiling at 154° – 157° . The hexyl alcohol obtained by the saponification of this acetate forms an aromatic oil boiling at 138° , and its oxidation by dilute chromic acid mixture leads to the formation of butyric acid, acetic acid, and perhaps a trace of propionic acid, or rather of the ethers of these acids. Moreover, the hexylene just mentioned is reconverted into an iodide by the action of strong hydriodic acid, and the alcohol obtained from this iodide likewise yields, by oxidation, butyric and acetic acids, which acids are also produced by oxidation of the hexylene itself.

These results, more especially the reaction of diethyl ethyl oxide with hydriodic acid, and the subsequent oxidation of the hexylene compounds, indicate that diethyl ethyl oxide is a hexylic ethylate or ethylic hexylate, represented by the formula,



and chlorethyl ethyl oxide is most probably represented by the formula,



ETHYL SULPHIDE and HYDROSULPHIDE. On the compounds of these bodies with titanous chloride, see TITANIUM.

See **ALLYLAMINE** (p. 61).

ETHYLAMINES. A concentrated aqueous solution of ethylamine may be dehydrated by potassium hydrate to such a degree that the potash suffers no further alteration by immersion in the remaining liquid. On distilling such a solution, ethylamine is at first evolved as gas, but very soon a liquid begins to pass over, and the entire distillation is completed before the temperature of the liquid rises to 75° . This liquid is probably a definite hydrate of ethylamine (Wallach, *Deut. Chem. Ges. Ber.* vii. 326).

Ethylamine heated to 100° in sealed tubes with an alcoholic solution of *methylene iodide*, yields, together with ethylamine hydriodide, the hydriodide of tetrethyl-tetramethene-tetramine $\left\{ \begin{smallmatrix} (C^2H^5) \\ (CH^2) \end{smallmatrix} \right\}_4 N^4$, which in the free state is a very volatile oily base, very soluble in all acids, but not forming crystallisable salts. The platinum-chloride, which is perfectly amorphous, has the composition $\left\{ \begin{smallmatrix} (C^2H^5) \\ (CH^2) \end{smallmatrix} \right\}_4 N^4.2HCl.PtCl^4$. The base is related to Butlerow's hexmethylenamine (1st *Suppl.* 826), but differs from it considerably in its properties (Julie Lermontoff, *Deut. Chem. Ges. Ber.* vii. 1252).

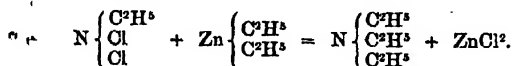
Action of Chloride of Lime on Ethylamine Hydrochloride (J. Teherniak, *Deut. Chem. Ges. Ber.* ix. 143).—The products of this reaction vary according to the quantity of bleaching powder used. If this quantity is not sufficient for the complete conversion of the ethylamine into dichlorethylamine (e.g. 4 or 5 parts of bleaching powder to 1 pt. of ethylamine hydrochloride) an oil is obtained which decomposes, even at ordinary temperatures, into a mixture consisting chiefly of hydrochloride and chlorate of ethylamine. On heating the crude product, nitrogen, chlorine,

and ethane are evolved, sometimes with explosive violence, and the chlorine exerts a decomposing action on the dichlorethylamine. The crude product, when quickly distilled, passes over for the most part between 75° and 95°, the distillate consisting of a mixture of chloroform and dichlorethylamine, while ethylamine hydrochloride remains behind.

Dichlorethylamine, $C^2H^5Cl^2N$. To prepare this base, ethylamine hydrochloride (100 grams) is added in portions of 25 grams to 250 grams of bleaching powder made into a thick cream with water, and the mixture is distilled so long as oily drops pass over. The product is again distilled with the same quantity of bleaching powder; the distillate is washed with water and shaken with an equal volume of dilute sulphuric acid (1 to 1); and the clear oily liquid which separates is washed with weak soda and with water, and dried over calcium chloride. By fractional distillation of this oily liquid a large quantity of pure dichlorethylamine, boiling at 88°–89°, is obtained. The pure substance is a clear, golden-yellow, highly refractive oil of extremely penetrating odour. Its sp. gr. is 1.2300 at 15°, and 1.2307 at 5°, water at the same temperatures being 1. At –30° it contracts considerably without solidifying. It may be kept indefinitely without alteration.

Action of Zinc-ethyl on Dichlorethylamine.—The pure substances react together with explosive violence. When the action is moderated by diluting both substances with ether and mixing them very gradually, the product is a mixture of ethylamine and triethylamine.

Since dichlorethylamine, by exchanging two atoms of chlorine for ethyl, yields triethylamine, it is evident that the chlorine contained in it must be combined directly with nitrogen, and the formation of triethylamine must be represented thus:—

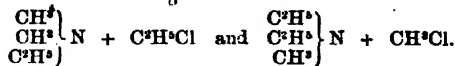


The formation of *ethylamine* in the foregoing reaction is explained by the peculiar position of the chlorine-atoms in dichlorethylamine, in virtue of which they possess a substituting capacity analogous to that of free chlorine, so that dichlorethylamine, in contact with many organic substances, such as acetic acid, ether, &c., is able to exchange its chlorine for hydrogen, thus regenerating ethylamine.

Triethylamine, $N(C^2H^5)^3$. On heating this base to 100° in sealed tubes with an alcoholic solution of *methylene iodide*, the liquid deposits crystals which, when recrystallised from alcohol, form colourless square plates, consisting of a compound of triethylamine and methylene iodide, $(C^2H^5)^3N \cdot CH_2I_2$, or iodomethyl-triethylamine iodide, $\begin{Bmatrix} C^2H^5 \\ CH_2I \end{Bmatrix}^3NI$. This last view of their constitution is supported by the fact that the compound, when heated in aqueous solution with recently precipitated silver chloride, exchanges only 1 atom of its iodine for chlorine. The resulting chlorinated compound forms with platinum chloride a double salt which crystallises in splendid octohedrons. It has not been found possible to obtain a base free from iodine by treating the iodide with silver oxide (Julie Lermoutoff, *Deut. Chem. Ges. Ber.* vii. 1272).

When triethylamine is heated with *ethyl chloropropionate* in sealed tubes for several hours to about 200°, triethylamine hydrochloride and tetrethylammonium chloride are produced, together with ethyl chloride and perhaps ethyl acrylate (Brühl, *Deut. Chem. Ges. Ber.* ix. 34).

On the identity of the compounds,



see AMMONIUM SALTS (p. 74).

ETHYL-AMYL, $C^2H^5 \cdot C^5H^{11}$. See HEPTANES (2nd Suppl. 642).

ETHYL-AMYL KETONE, $C^2H^5 \cdot CO \cdot C^5H^{11}$. See KETONES and PINACOLINS.

$\begin{array}{c} C^6H^5-N \\ | \\ (C^2H^5)_2N-C=O \end{array} \cdot C^6H^5N^2 =$ The hydriodide of this base is formed, together with another compound, by heating anhydrosbenzoyl-diamidobenzene, $C^6H^5N^2$ (see BENZANILIDE,

p. 104), with excess of ethyl iodide to 180°. The free base is moderately soluble in water; the hydrochloride and the basic sulphate crystallise in needles.

Amyl-anhydrosenoyl-diamidobenzene, $C^{10}H^{10}N^2$, obtained in like manner, crystallises from alcohol in microscopic rhombic plates melting at 270°. Its salts are crystallisable (Seanewald, *Deut. Chem. Ges. Ber.* ix. 775).

ETHYLANILINE, $C^6H^5.NH.C^2H^5$. See ETHYLAMIDOBENZENE under BENZENE (p. 205).

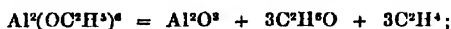
ETHYLANILINE-SULPHONIC ACID, $C^6H^4 \begin{smallmatrix} \text{NH}(C^2H^5) \\ \text{SO}^3H \end{smallmatrix}$. See BENZENE-SULPHONIC ACIDS (p. 235).

ETHYLANISYDROXAMIC ACID. See HYDROXAMIC ETHERS.

ETHYLATES *Aluminium Ethylate*, $Al(OC^2H^5)^3$ or $Al^3(OC^2H^5)^3$. Alcohol is not decomposed by aluminium alone, even when boiled with it for several hours, but when aluminium-foil is added to a solution of aluminium iodide in absolute alcohol, or of iodine in absolute alcohol (whereby aluminium iodide is formed in the first instance), reaction sets in at ordinary temperatures, after about half-an-hour in the first case, immediately in the second, hydrogen being evolved equivalent to the quantity of aluminium not combined with iodine, and a greyish-white pasty residue being left, consisting of aluminium ethylate mixed with a small quantity of aluminium iodethylate, which is decomposed on heating the residue to 275°, according to the equation,



The aluminium ethylate is at the same time decomposed into aluminium, alcohol, and ethylene gas:

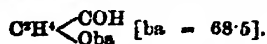


but, on heating it to about 270° under diminished pressure, it distils for the most part without decomposition; condensing in the form of a yellowish white solid, while only a small quantity of alumina (equivalent to the decomposition of 10 per cent. of the ethylate) remains behind.

Aluminium ethylate dissolves slightly in absolute alcohol, and water added to the solution throws down aluminium hydrate. Hot water decomposes it rapidly, forming alcohol and aluminium hydrate. It melts at 115°, and boils somewhat above the range of the mercurial thermometer. Exposed to the air at ordinary temperatures, it quickly decomposes, yielding alumina, and doubtless also alcohol.

Aluminium ethylate affords the second instance of an oxygenated organo-metallic body capable of distillation, the only such body previously known being cacodylic acid (Gladstone & Tribe, *Chem. Soc. J.* 1876, i. 160).

Barium Ethylate, $C^2H^5BaO^2 = Ba(OC^2H^5)^2$ (Berthelot, *J. pr. Chem.* [2], viii. 22). Barium ethylate is prepared by adding anhydrous baryta to commercial absolute alcohol, and leaving it to stand over night. The liquid, which does not contain any baryta, is then filtered under a bell-jar, and again left in contact with baryta for some hours. The yellow solution thus obtained is at once precipitated by adding a very small quantity of water. On distilling this liquid, perfectly absolute alcohol passes over, and barium alcoholate separates out. This compound is much more soluble in cold than in hot alcohol, and is obtained pure by decanting the hot liquid, and drying the residue in the retort at 100°, in a current of pure hydrogen. Its alcoholic solution slowly absorbs carbon monoxide at ordinary temperatures, forming the compound $C^2H^5BaO^4$, which has the composition of barium propionate, but differs from that compound by being soluble in alcohol and readily decomposed by water. Berthelot regards it as 'ethyl-formate' of barium; but this designation affords no indication of its isomerism with the propionate, inasmuch as ethyl-formic acid is identical with propionic. Kolbe (*ibid.* 27) suggests that it may be the *formyl-ethylate of barium*:



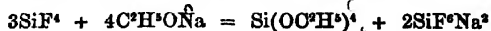
Sodium Ethylate, C^2H^5ONa .—This compound, when heated, partly splits up into ethylene and sodium hydroxide, but the latter acts upon other portions of the ethylate, forming sodium acetate and humus-like bodies (Merz & Weith, *Deut. Chem. Ges. Ber.* vi. 1517).

With bromine, not in excess, sodium ethylate forms alcohol, together with bromide acetate, and monobromacetate of ethyl; but with excess of bromine, the chief product is dibromethylene bromide, $C^2H^2Br^2$, accompanied by formic acid, acetic acid, alcohol, and ethyl monobromacetate (Sell & Salzmann, *Deut. Chem. Ges. Ber.* vii. 496).

750 ETHYL-BENZENE ALCOHOL—ETHYL-CROTONIC ACID.

According to M. Barth, on the other hand (*ibid.* ix. 1455), when bromine vapour is made to act on sodium ethylate, well dried in a stream of hydrogen at 180°, and afterwards cooled by a mixture of snow and salt, the products consist of bromal, ethyl bromide and ethyl acetate, together with hydrogen bromide, sodium bromate, and sodium bromide.

With *silicon fluoride*, sodium ethylate forms tetrethylic silicate, and sodium silico-fluoride:



(Klippert, *Deut. Chem. Ges. Ber.* viii. 713).

On the reactions of Sodium Ethylate with *Chlorides*, see 2nd Suppl. 486; with *Ethyl acetate* and its derivatives, see ACETO-ACETIC ETHERS, p. 13 of this volume; with *Morphine* and *Codeine*, see these bases.

ETHYL-BENZENE ALCOHOL, SECONDARY. $\text{C}^2\text{H}^5\text{—CHOH—CH}^3$.
See PHENYL ALCOHOLS.

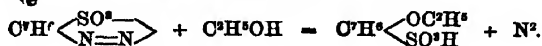
ETHYL-BENZENE-SULPHONIC ACIDS, $\text{C}^2\text{H}^5\text{SO}^3\text{H}$. Two acids having this composition are obtained by digesting ethyl-benzene with fuming sulphuric acid at the heat of the water-bath. On treating the product with potash, two potassium salts are obtained, the more abundant and less soluble of which crystallises well. This salt, when fused with potassium hydrate, yields chiefly solid ethyl-phenol, $\text{C}^2\text{H}^5(\text{C}^2\text{H}^5)\text{OH}$; the chloride obtained from it forms, with ammonia, a crystallisable amide melting at 108°. The other potassium salt, which is much more soluble but likewise crystallisable, yields a crystallisable amide having a lower melting point. The existence of these two ethyl-benzene-sulphonic acids explains the formation of two isomeric ethyl-phenols from potassium ethyl-benzene-sulphonate, observed by Beilstein a. Krhlberg (*Liebig's Annalen*, clvi. 211).

ETHYL-BENZHYDROKAMIC ACID. See HYDROXAMIC ETHERS.

ETHYL-BUTYL PINACOLIN. See PINACOLINS.

ETHYL-CARBOXYLAMINE, $\text{CO=N—C}^2\text{H}^5$. A compound supposed by v. Zotta to be formed in the decomposition of diethyl-carbamide by nitrous acid (p. 390).

ETHYL-CRESOLSULPHONIC ACID, $\text{C}^2\text{H}^5\left\{\begin{smallmatrix} \text{OC}^2\text{H}^5 \\ \text{SO}^3\text{H} \end{smallmatrix}\right.$, is formed by the action of absolute alcohol on diazoparatoluenesulphonic acid:

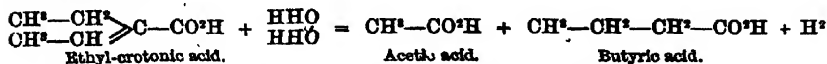


The *potassium salt*, $\text{C}^2\text{H}^5\cdot\text{OC}^2\text{H}^5\cdot\text{SO}^3\text{K} + \text{H}^2\text{O}$, forms white nacreous needles grouped in thin leaflets; it dissolves very easily in water, with moderate facility in alcohol, and becomes anhydrous when left over sulphuric acid. The *barium salt*, $(\text{C}^2\text{H}^5\cdot\text{OC}^2\text{H}^5\cdot\text{SO}^3)^2\text{Ba} + 3\text{H}^2\text{O}$, forms very small needles easily soluble in hot, sparingly in cold water. The *lead salt*, $(\text{C}^2\text{H}^5\cdot\text{OC}^2\text{H}^5\cdot\text{SO}^3)^2\text{Pb} + 3\text{H}^2\text{O}$, crystallises in tufts of slender needles, and, like the barium salt, does not give off any of its water over sulphuric acid.

Ethylcresolsulphonic acid, when fused with potash, is converted, not into ethyl-salicylic but into salicylic acid (Hayduck, *Liebig's Annalen*, clxxiv. 343).

ETHYL-CROTONIC ACID, $\text{C}^2\text{H}^5(\text{C}^2\text{H}^5)\text{C}^2$. On the formation of this acid from isocaproic acid, and its conversion into that acid, see CAPROIC ACIDS (p. 379).

The butyric acid, formed, together with acetic acid, by fusion of ethyl-crotonic acid with potash (1st Suppl. 42), has been found, from the amount of water of crystallisation of its calcium salt, and the relations of that salt to various solvents, to be normal butyric acid (2nd Suppl. 226). This mode of decomposition of ethyl-crotonic acid establishes the correctness of the constitutional formula $\text{CH}^3\text{—CH}^2\text{—CH}^2\text{—CH}^2\text{—CO}^2\text{H}$, deduced from its mode of formation from diethoxalic acid (1st Suppl. 42):



There are five other possible modifications of the acid $\text{C}^2\text{H}^5\text{O}^2$, capable of yielding, by fusion with a caustic alkali, acetic acid and either normal butyric or isobutyric acid. Of these, however, only one is positively known, viz. pyroterebic acid,

$(\text{OH})^{\text{a}}\text{CH}=\text{CH}=\text{CH}-\text{CO}^{\text{a}}\text{H}$, which yields isobutyric acid. Hydrosorbic acid (2nd Suppl. 1092) may perhaps be another of these modifications, although when fused with potash it yields merely butyric without acetic acid (Petrieff, *Deut. Chem. Ges. Ber.* vi. 1098).

ETHYL-DIACETIC ACID, syn. with ETHYLIC ACETO-ACETATE. See ACETO-ACETIC ETHERS (p. 12).

ETHYL-DICRESTYLAMINE, $\text{N}(\text{C}^{\text{a}}\text{H}^{\text{a}})(\text{C}^{\text{a}}\text{H}^{\text{a}}.\text{CH}^{\text{a}})^{\text{a}}$, syn. with ETHYL-DI-TOLYLAMINE. See TOLYLAMINES.

DIETHYLSULPHONIODIDE-ACETATE. See SULPH-ACETIC ACIDS.

IDE, $\text{CO.C}(\text{C}^{\text{a}}\text{H}^{\text{a}})(\text{OH})^{\text{a}}\text{Cl}$, is prepared by treating 1 mol. ethyl-dimethylacetic acid (p. 379) with 1 mol. PCl^{a} , and

methyl-amyl ketone, $\text{CH}^{\text{a}}-\text{CO}-\text{C}^{\text{a}}\text{H}^{\text{a}}$, and with zinc-ethyl, ethylamyl ketone, $\text{C}^{\text{a}}\text{H}^{\text{a}}-\text{CO}-\text{C}^{\text{a}}\text{H}^{\text{a}}$ (Wischnegradsky, *Liebig's Annalen*, clxxviii. 103).

ETHYL-BENZENE. The symmetrical modification of this hydrocarbon, $\text{C}^{\text{a}}.\text{C}^{\text{a}}\text{H}^{\text{a}}.\text{H}.\text{OH}^{\text{a}}.\text{H}.\text{CH}^{\text{a}}.\text{H}$, may be prepared as follows: An alcoholic solution of bromoxylinide, treated with nitrous acid, yields a bromoxylene or bromo-dimethyl-benzene, $\text{C}^{\text{a}}\text{H}^{\text{a}}(\text{OH}^{\text{a}})^{\text{a}}\text{Br}$, boiling at 204° and remaining liquid at -20° , and a mixture of this bromoxylene and ethyl bromide, heated with sodium, yields a hydrocarbon, $\text{C}^{\text{a}}\text{H}^{\text{a}}(\text{C}^{\text{a}}\text{H}^{\text{a}})(\text{CH}^{\text{a}})^{\text{a}}$, which has a density of 0.861, boils at 185° , and remains fluid at -20° . This hydrocarbon, oxidised with dilute nitric acid, yields oxyvinic acid, $\text{C}^{\text{a}}\text{H}^{\text{a}}(\text{OH}^{\text{a}}\text{OH})(\text{CO}^{\text{a}}\text{H})^{\text{a}}$, and mesitylenic acid, $\text{C}^{\text{a}}\text{H}^{\text{a}}(\text{OH}^{\text{a}})^{\text{a}}\text{CO}^{\text{a}}\text{H}$, both of which have their substituted radicles in the relative positions 1 : 3 : 5; hence the hydrocarbon itself is symmetrical ethyl-dimethyl-benzene (Wroblewsky, *Deut. Chem. Ges. Ber.* ix. 495).

ETHYL-DIMETHYLPHOSPHONIUM HYDROXIDE. See PHOSPHORUS-BASES.

ETHYL-DIPHENYLAMINE, $\text{N}(\text{C}^{\text{a}}\text{H}^{\text{a}})(\text{C}^{\text{a}}\text{H}^{\text{a}})^{\text{a}}$. See BENZENES, PHENYL-AMIDO- (p. 208).

ETHYL-DIPHENYL-GUANIDINE, $\text{N}^{\text{a}}\text{CH}^{\text{a}}(\text{C}^{\text{a}}\text{H}^{\text{a}})(\text{C}^{\text{a}}\text{H}^{\text{a}})^{\text{a}}$. See GUANIDINE.

ETHYLENE or **ETHENE**, $\text{C}^{\text{a}}\text{H}^{\text{a}}=\text{H}^{\text{a}}\text{C}=\text{CH}^{\text{a}}$. Erlenmeyer & Bunte (*Liebig's Annalen*, clxviii. 64) prepare this hydrocarbon by heating 25 grams of alcohol and 150 grams of sulphuric acid in a flask of 2 or 3 litres capacity placed on a sand-bath, and gradually dropping in a mixture of equal parts of alcohol and sulphuric acid. The contents of the flask quickly blacken, but very little frothing takes place.

Reactions. 1. With *Oxygen*.—When a mixture of ethylene and air is passed over red-hot platinum wire, the ethylene is partly oxidised to acetic acid* (Coquillion, *Compt. rend.* lxxvii. 444).

A mixture of ethylene with strongly ozonised oxygen (at least 60 mgrm. in a litre) detonates violently, and without the aid of light, heat, or electricity. When ethylene is slowly oxidised by weakly ozonised oxygen, formic acid and carbon dioxide are produced, together with thick white fumes which are completely absorbed by strong sulphuric acid (Houzeau & Renard, *ibid.* lxxvi. 572).

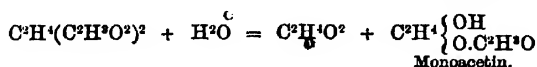
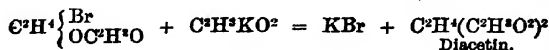
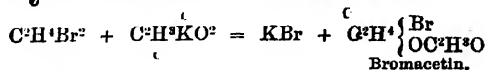
On the imperfect combustion of Ethylene by explosion with insufficient quantities of Oxygen, see p. 436.

2. With *Hydrogen*.—Ethylene, mixed with hydrogen in contact with platinum, takes up H^{a} , and is converted into ethane, $\text{C}^{\text{a}}\text{H}^{\text{a}}$ (v. Wilde, *Deut. Chem. Ges. Ber.* vii. 362f).

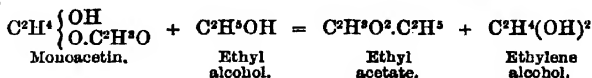
3. With *Hydrocarbons*.—A mixture of ethylene and diphenyl, passed through a porcelain tube heated to bright redness, yields a mixture of phenanthrene and anthracene, the former predominating, together with benzene, cinnamene, and naphthalene, the reaction therefore taking place partly as represented by the equation, $\text{C}^{\text{a}}\text{H}^{\text{a}} + \text{C}^{\text{a}}\text{H}^{\text{a}} = \text{C}^{\text{a}}\text{H}^{\text{a}} + 2\text{H}^{\text{a}}$. Phenanthrene and anthracene are also found amongst the products which Berthelot obtained by the action of ethylene on benzene (Barbier, *Compt. rend.* lxxix. 121).

4. With *Phosphine*.—A mixture of this gas with ethylene, subjected to the action of the silent electric discharge, yields an alcoholic phosphine (P. and A. Thénard, *ibid.* lxxvi. 1508).

ETHYLENE ALCOHOL. *Glycol*, $C^2H^4O^2 = C^2H^4(OH)^2$.—This compound is formed in considerable quantity when ethylene dibromide and potassium acetate in equal numbers of molecules are heated to boiling for eighteen hours with alcohol of 91 per cent., or for forty hours with alcohol of 80 per cent. The reaction appears to take place in the manner represented by the following equations:



and finally,



When ethylene bromide and potassium acetate are heated together to 150° – 200° for two days, ethylene diacetate is produced, but no glycol; and ethylene bromide and monoacetin may be boiled together for eighteen hours without formation of any new products (Demole, *Liebig's Annalen*, clxxiii. 117; clxxvii. 45; *Deut. Chem. Ges. Ber.* vii. 641; viii. 1; *Chem. Soc. Jour.* 1875, 747, 1172).

Zoller and Hüfner (*J. pr. Chem.* [2], x. 270) obtain perfectly pure glycol by heating 1 mol. ethylene bromide with 1 mol. potassium carbonate dissolved in water, for ten hours in a flask fitted with a reversed condenser. The glycol thus prepared boiled at 194° ; see also Lietzenmayer (*Liebig's Annalen*, clxxx. 282; *Chem. Soc. Jour.* 1876, ii. 64).

According to Grosheintz (*Bull. Soc. Chim.* [2], xxviii. 57), the carbon dioxide evolved in this process is accompanied by a large proportion of monobromethylene, whereby the theoretical yield of glycol is greatly diminished.

Glycol unites energetically with *chloral*, and the resulting compound, treated with phosphorus pentachloride, yields a body having the composition $CCl^3-CH \begin{Bmatrix} O \\ Cl \end{Bmatrix} -CH^2-CH^2-O \begin{Bmatrix} O \\ Cl \end{Bmatrix} -CH-Cl^3$. This compound is a viscid liquid having a sp. gr. of 1.73 at 13° , and decomposing when distilled (*L. Henry, Deut. Chem. Ges. Ber.* vii. 762).

ETHYLENE BROMIDE, CH^2Br-CH^2Br . This compound, boiling at 131° , is formed, together with bromomethyl bromide, CH^3-CHBr^2 (b. p. 114°), and dibromomethyl bromide, $CH^2Br-CHBr^2$, by the action of bromine on ethyl bromide. The first two may be completely separated from one another by potassium hydroxide, the bromomethyl bromide remaining unaltered, while the ethylene bromide is converted into ethylene hydrosulphide or glycolic mercaptan, C^2H^4S (Tawildarow, *Deut. Chem. Ges. Ber.* vi. 1459).

For the preparation of ethylene bromide, Erlenmeyer and Bunte (*Liebig's Annalen*, clxviii. 64) make use of an apparatus in which the ethylene gas, generated by heating alcohol with sulphuric acid, passes through a series of four Woulfe's bottles, the first empty, the second containing sulphuric acid, and the third and fourth potash or soda-ley; next through the tube of a reversed Liebig's condenser; and finally into a Woulfe's bottle containing bromine, whereby it is absorbed, this vessel being connected with a sixth Woulfe's bottle filled to a height of four or five inches with fragments of glass, and thence up to the shoulder with granulated soda-lime. By blowing air into this last bottle, a quantity of bromine is forced into the condensing tube sufficient to fill it one-half, and the condensing tube is then attached to the generating apparatus, after a sufficient quantity of ethylene has been evolved to expel all the air from the latter. With this apparatus from 1000 to 1100 grams of ethylene bromide may be prepared in seven hours.

On the action of Ethylene bromide on Potassium acetate, see p. 752. On its decomposition by the Copper-zinc couple (2nd Suppl. 489).

A compound having the formula $C^2H^2Br^4$, probably dibromomethylene dibromide, $C^2H^2Br^2.Br^2$, is formed when ordinary pyrotartaric acid is heated with bromine and water in a sealed tube for six hours at 122° (Bourgoin, *Compt. rend.* lxxxiv. 776).

ETHYLENE BROMODIDE—ETHYLENE CHLORIDE. 758

On tetrabromethylene hydride, or tetrabromethane, and its isomerism with acetylene tetrabromide, see ACETYLENE (p. 35).

C^2H^2BrI . Two of these compounds, one boiling at 141° – 142° , the other at 162° , were prepared by Reboul by the action of hydriodic acid on monobromethylene, C^2H^2Br (2nd Suppl. 489). Lagermark (*Deut. Chem. Ges. Ber.* vi. 1211; vii. 967) and Maxwell Simpson (*Proc. Roy. Soc.* xxii. 81) have obtained a third modification by passing ethylene gas into a solution of iodine in bromine (prepared by adding more than 1 mol. finely-powdered iodine to bromine diluted with 6 parts of water, stirring briskly and keeping the liquid cool, and separating the solution from undissolved iodine by decantation (Simpson). From this solution the ethylene bromiodide crystallises in long white needles, having a density of 2.516 at 29° , melting at 28° , and boiling between 162° and 167° (Simpson). Lagermark's product, probably impure, melted at 25.5° and boiled at 150° .

By the action of an alcoholic solution of sodium acetate, this bromiodide is converted into ethylene acetioldhydrin, $C^2H^2(C^2H^3O^2)$ (Lagermark).

Lagermark finds that Reboul's lower-boiling bromiodide (141° – 142°) is best prepared by treating vinyl bromide with dry gaseous hydrogen iodide, instead of the aqueous acid as recommended by Reboul. For this purpose a quantity of phosphorus tri-iodide is shaken into a strong glass tube sealed at one end, and above it is placed a glass bulb containing a quantity of water sufficient to decompose it, and a small test tube into which the required quantity of vinyl bromide is introduced by means of a tube-funnel. The strong glass tube is then drawn out to a point, sealed, and plunged into a freezing mixture, whereupon the bulb containing the water bursts, hydriodic acid is generated, and the action on the vinyl bromide commences. The tube is then removed from the freezing mixture, and the action continued at the ordinary temperature. The product decolorised by potash, dried, and once distilled, yields the pure bromiodide as a slightly yellow liquid, having a density of 2.452 at 16° , and boiling at 142° – 143° . By bromine it is converted into brominated ethyl bromide, $CH^2=CHBr$, and by alcoholic potash, into potassium iodide and vinyl bromide, $CH^2=CHBr$, whence it appears to consist of ethyldene bromiodide, $CH^2=CHBr$.

The higher-boiling bromiodide (162°) described by Reboul does not appear to be a definite compound; see Gagarin (*Deut. Chem. Ges. Ber.* vii. 733), and Butlerow (*ibid.* 734, 1456), also *Chem. Soc. J.* 1874, 1076.

ETHYLENE CHLORHYDRIN, $C^2H^2Cl(OH) = CH^2Cl-CH^2OH$. This compound, treated with bromine, yields ethylene chlorobromide, mono- and dibrom-acetic acid, ethylene bromide, ethylene bromhydrin, and probably also ethylene brom-acetobromhydrin, $C^2H^2Br(OC^2H^3BrO)$. Some of these products appear to be due to the action of hydrobromic acid, formed in the first instance by the action of the bromine: for ethylene chlorhydrin directly treated with hydrobromic acid yields ethylene bromide, ethylene chlorobromide, and ethylene bromhydrin (together with ethylene chloride). The formation of the bromacetic acids by the action of bromine on ethylene chlorhydrin is for the present unexplained (Demole, *Deut. Chem. Ges. Ber.* ix. 1876).

Ethylene chlorhydrin unites with chloral, forming a body represented by the formula $CCl^2-CH \begin{smallmatrix} O-CH^2-CH^2Cl \\ \diagdown \\ OH \end{smallmatrix}$. It is a thick viscid liquid, which does not solidify in a freezing mixture, and undergoes dissociation when heated. With acetyl chloride it forms an acetyl-derivative, $CCl^2-CH \begin{smallmatrix} O-CH^2-CH^2Cl \\ \diagdown \\ O-C^2H^3O \end{smallmatrix}$; and with PCl^3 , a chloride, $CCl^2-CH \begin{smallmatrix} O-CH^2-CH^2Cl \\ \diagdown \\ Cl \end{smallmatrix}$, in the form of a clear colourless liquid, having a pungent camphorous odour and sweetish taste, a sp. gr. of 1.577 at 8° ; boiling without decomposition at 235° ; insoluble in water, easily soluble in alcohol and ether (L. Henry, *Deut. Chem. Ges. Ber.* vii. 762).

Ethylene Acetochlorhydrin, $C^2H^2 \begin{smallmatrix} Cl \\ \diagup \\ OC^2H^3O \end{smallmatrix}$, is formed by heating ethylene chlorhydrin to 110° for five or six hours with $1\frac{1}{2}$ pt. glacial acetic acid. The product, after washing with water and with soda-ley, and drying over potassium carbonate, distilled for the most part between 143° and 145° (Ladenburg a. Demole, *ibid.* vi. 1023).

ETHYLENE CHLORIDE, $C^2H^2Cl^2$, heated to 170° for several hours with lead oxide and water, yields lead chloride, ethylene glycol, and traces of ethylene oxide (Jeltkow, *ibid.* vi. 558).

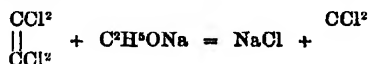
Chloroethylenes. **Perchloroethylene**, C^2Cl^4 , may be prepared by dissolving 3rd Sup. 3 C

carbon trichloride or hexachlorethane, C^2Cl^4 , in twice its weight of aniline, and heating the solution in a retort to 170° . The distillate, consisting of perchlorethylene with a little aniline and carbon trichloride, is redistilled with an equal weight of aniline at 130° – 145° , and the new distillate is freed from admixed aniline by washing with dilute sulphuric acid and with water. Pure perchlorethylene boils at 121° , and has a sp. gr. of 1.6595 at 0° (Bourgoin, *Compt. rend.* lxxx. 971).

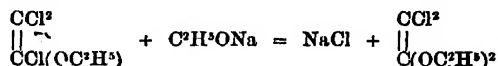
Perchloroethylene Dibromide, $\text{C}^2\text{Cl}^2\text{Br}^2$, formed by direct bromination of perchlorethylene, is isomeric with dichloroacetylene chlorobromide, $\text{C}^2\text{Cl}^2\left\{\begin{smallmatrix} \text{Br}^2 \\ \text{Cl}^2 \end{smallmatrix}\right.$, formed by the action of chlorine on acetylene tetrabromide (p. 36). The latter, when heated to 185° , first gives off half its chlorine, and is converted into $\text{C}^2\text{Cl}^2\text{Br}^2$; but on raising the temperature a little higher, the free chlorine is reabsorbed, and the bromine driven out, the final result being the formation of perchlorethylene, C^2Cl^4 . Perchloroethylene dibromide, on the other hand, is directly resolved by heat into Br^2 and C^2Cl^4 .

When the two isomeric bromides are heated with a mixture of aniline and toluidine, the first to 150° , the second to 170° , the perchlorethylene dibromide is converted, with formation of rosaniline hydrochloride, into chlorobromomethylene, $\text{C}^2\text{Cl}^2\text{Br}^2$, which is a colourless liquid smelling like chloroform, solidifying at -16° , and boiling at about 130° . It unites with bromine, forming a crystalline bromide, $\text{C}^2\text{Cl}^2\text{Br}^2\cdot\text{Br}^2$. (Bourgoin, *Compt. rend.* lxxxi. 48).

Action of Sodium Ethylate on the Chlorethylenes.—Geuther a. Fischer, in 1864, by treating perchlorethylene with sodium ethylate, obtained an oily liquid, consisting mainly of ethylic dichloroacetate with a small quantity of dichloroacetic chloride, and a body soluble in water, consisting of the sodium salt of ethyl-glyoxylic acid (1st Suppl. 19); the formation of these products is explained as follows by Geuther a. Brockhoff (*Jenaische Zeitschr. f. Naturwissenschaft.* vii. 359). The first product of the reaction is trichlorethoxyl-ethylene, derived from perchlorethylene by substitution of 1 at. OC^2H^3 for 1 at. Cl :



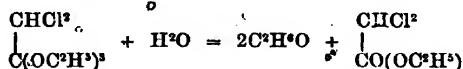
This compound is converted, by the further action of the sodium ethylate, into dichloroethylethylene,



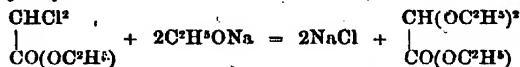
which, by taking up the elements of alcohol, is converted into triethylic dichloroacetate,



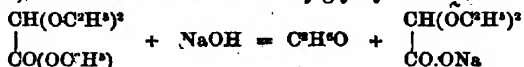
and this last compound is converted by the action of water—which is formed in the reaction together with brown resinous substances—into monethylic dichloroacetate,



This ether reacts with sodium ethylate, in such a manner as to form the ethylic ether of diethylglyoxylic acid:



which is finally converted, by the action of caustic soda (produced by water from the sodium ethylate), into the sodium salt of diethylglyoxylic acid:



The formation of the intermediate products above mentioned has been demonstrated by experiments in which the action of the sodium ethylate was more or less limited; and it has further been shown that the quantity of trichlorethoxyl-ethylene obtained is greater in proportion as the reaction takes place at a lower temperature, and is

ETHYLENE-BASES—ETHYLENE-DISULPHONIC ACID. 755

continued for a shorter time; also that trichlorethoxyl-ethylene is easily converted by alcoholic sodium ethylate into the sodium salt of ethoxylglycollic acid.

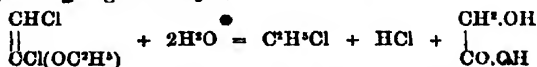
Perchlorethylene, treated with sodium ethylate free from alcohol, yields the same products as above, but in smaller quantity; a gas burning with a blue flame is also given off.

Trichlorethylene Chloride, $\text{C}^2\text{H}^2\text{Cl}^3\cdot\text{Cl}^3$ or $\text{OCl}^3-\text{CHCl}^3$, prepared by the action of chlorine on ethylene chloride in bright daylight, acts upon sodium ethylate either dry or dissolved in alcohol, forming perchlorethylene, ethyl alcohol, and sodium chloride (Geuther a. Brockhoff).

Dichlorethylene Dichloride, $\text{C}^2\text{H}^2\text{Cl}^2\cdot\text{Cl}^2$ or $\text{CHCl}^2\cdot\text{CHCl}^2$ (prepared in the same manner as the preceding compound and boiling at 135°F (corr.)), acts very strongly on alcoholic sodium ethylate, forming dichlorethoxyl-ethylene, $\text{C}^2\text{HCl}^2(\text{OC}^2\text{H}^3)$.

Monochlorethylene Chloride, $\text{C}^2\text{H}^3\text{Cl}\cdot\text{Cl}^2$ or $\begin{array}{c} \text{CH}^2\text{Cl} \\ | \\ \text{CHCl}^2 \end{array}$, and excess of sodium ethylate, either dry or alcoholic, yield chiefly dichlorethylene, $\text{C}^2\text{H}^2\text{Cl}^2$, and a small quantity of acetic acid.

Dichlorethoxyl-ethylene, $\text{CHCl}^2=\text{CCl}(\text{OC}^2\text{H}^3)$, is a colourless liquid having a peculiar taste with pungent after-taste, a sp. gr. of 1.08 at 10° , boiling at 128.2° (corr.). It may be washed with water without alteration, but decomposes gradually on exposure to moist air. When heated to 100° with water, it yields glycollic acid, ethyl chloride, and hydrogen chloride:



By an excess of alcoholic sodium ethylate, it is converted into sodium ethoxyl-glycolate, ethylic monochloracetate being however apparently formed as an intermediate product (Geuther a. Brockhoff). When dichlorethoxyl-ethylene is treated with a quantity of sodium ethylate considerably less than that which is required to decompose the whole of it, ethoxylglycollic acid is likewise formed, together with ethyl chloride, ethyl monochloracetate, and hydrochloric acid.

ETHYLENE-BASES. According to A. Gretillat (*Monit. scient.* [3], iii. 383), ethylene-diphenyldiamine, $\text{N}^2(\text{C}^6\text{H}^5)^2(\text{C}^2\text{H}^4)\text{H}^2$, prepared by treating ethylene bromide with a large excess of aniline (iv. 455), is always mixed with diethylene-diphenyl-diamine, $\text{N}^2(\text{C}^6\text{H}^5)^2(\text{C}^2\text{H}^4)^2$, but may be separated therefrom by dissolving the mixture in boiling strong acetic acid, and adding alcohol, whereupon the diethylene-base separates in crystals.

The two free hydrogen-atoms in ethylene-diphenyl-diamine may be replaced by acid radicles, either of the fatty or of the aromatic groups. *Ethylene-diacyetyl-diphenyl-diamine* is a crystalline body, easily soluble in boiling alcohol and in ligroin, and still exhibiting basic properties, in *ethylene-dibenzoyl-diphenyl-diamine*, on the other hand, the basic character is absent.

Ethylene-ditolyl-diamine, $\text{N}^2(\text{C}^6\text{H}^4\cdot\text{CH}^3)(\text{C}^2\text{H}^4)\text{H}^2$, and triethylene-tritolyl-triamine, $\text{N}^3(\text{C}^6\text{H}^4\cdot\text{CH}^3)^3(\text{C}^2\text{H}^4)^3$, are formed simultaneously by the action of ethylene bromide on toluidine at 150° in a capacious flask fitted with a reflux condenser, and may be separated by means of alcohol, in which the former is freely, the latter very sparingly soluble. The *triethylene-base*, when pure, crystallises in splendid needles melting at 186° . Its hydrochloride forms needles melting at 189° . The *diethylene-base* is difficult to purify, on account of its easy solubility; it must be purified by separation from its salts. It forms crystals melting at 97.5° . Its hydrochloride crystallises in long white needles easily soluble in boiling water (Gretillat).

ETHYLENE-DISULPHONIC ACID, $\text{C}^2\text{H}^2(\text{SO}^3\text{H})^2$, is formed by dissolving nitroethane in cooled fuming sulphuric acid, and then gently warming the mixture, whereupon a brisk evolution of gas takes place. If, when this action is over, the liquid be carefully poured into water, neutralised with barium carbonate, and filtered hot, the filtrate on cooling will deposit barium ethylene-disulphonate. The *lead salt*, $\text{C}^2\text{H}^2(\text{SO}^3)^2\text{Pb} + 2\text{H}^2\text{O}$, forms scaly crystals (Meyer a. Wurster, *Deut. Chem. Ges. Ber.* xi. 1168; *Jahresb. f. Chem.* 1873, 302).

Ethylene-disulphonic Chloride, $\text{C}^2\text{H}^2(\text{SO}^3\text{Cl})^2$, is formed by the action of 2 mol. phosphorus pentachloride on 1 mol. potassium ethyldisulphonate. The crude product is poured into water, and the substance, which solidifies, for the most part, after a short time, is freed from adhering phosphorus oxychloride by draining on porous plates, and recrystallised from anhydrous ether. The chloride crystallises in

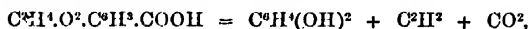
needles melting at 91°, is not much attacked by cold water, but cannot be distilled without decomposition. At 150° it carbonises, with evolution of hydrochloric and sulphurous acids, and, when boiled with alcohol, gives off ethyl chloride and sulphurous acid. On heating it to 150°–160° for several hours in sealed tubes with 1 mol. phosphorus oxychloride, and subjecting the contents to fractional distillation under a pressure of about 30 mm., phosphorus pentachloride passes over first, then at 125°–127° dichloroethylthion chloride, $C^2H^4Cl_2SO_2Cl$. This latter is slowly attacked by phosphorus pentachloride (1 mol.) at 200°, ethylene chloride being formed among the products (W. König, *Deut. Chem. Ges. Ber.* vii. 1163).

ETHYLENE-LACTIC ACID. See LACTIC ACID.

ETHYLENE-PROTocatechuic ACID, $C^2H^4O^4 = C^2H^4\langle\begin{smallmatrix} O \\ \diagup \diagdown \end{smallmatrix}\rangle C^2H^4-COOH$ (Fittig a. Macalpine, *Liebig's Annalen*, clxviii. 99). This acid, homologous with piperonylic acid, is obtained by treating protocatechuic acid with ethylene bromide and solid potash, and separates from water in colourless indistinct crystals, from alcohol in druses of short shining prisms (2nd *Suppl.* 1024).

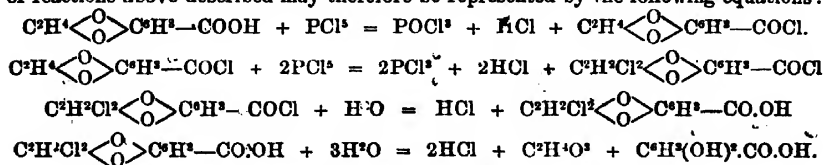
Calcium Ethyleneprotocatechuate, $(C^2H^4O^4)Ca + 2H^2O$, crystallises with great facility, in monoclinic crystals having the axial ratio $a : b : c = 0.654 : 1 : 0.667$; it gives off its water at 160°.

When ethylene-protocatechuic acid is heated in a sealed tube with dilute hydrochloric acid, decomposition begins at 260°, and the contents of the tube, which present the same appearance as in the corresponding experiment with piperonylic acid (1st *Suppl.* 949), yield a small quantity of pyrocatechin. Nevertheless, the reaction does not take place according to the equation



as might be expected from the mode of decomposition of piperonylic acid under similar circumstances (*loc. cit.*), for no acetylene could be detected in the gases evolved.

When ethylene-protocatechuic acid (1 mol.) is heated with phosphorus pentachloride (8 mols.) under ordinary pressure, a large portion of it remains unattacked and distils over together with phosphorus oxychloride; and the residue yields to cold water an oil which does not completely solidify, and dissolves in boiling water, the solution, on cooling, depositing a large quantity of ethylene-protocatechuic acid, whilst a small quantity of protocatechuic acid remains in the mother-liquid. These results show that the chief product of the reaction of PCl^5 on the acid is ethylene-protocatechuic chloride, $C^2H^4O^4.C^2H^4.COCl$, together with a small quantity of another chloride which is converted by boiling with water into protocatechuic acid. To obtain this latter chloride pure, the decomposition was repeated with the same proportions of material in a tube which was sealed after the first reaction, and then heated to 130° till no more phosphorus pentachloride separated on cooling. On pouring the product into cold water, a permanently liquid oil was obtained, which was converted by boiling with water into pure protocatechuic acid, and when heated with water to 100° for several hours in a sealed tube, yielded, together with protocatechuic acid, a solid acid, insoluble in water, melting at 118°–121°, having the composition of dichlorethyleneprotocatechuic acid, $C^2H^2Cl^2O^4.C^2H^4.CO^2H$, and resolved by boiling with water, into hydrochloric, protocatechuic, and possibly glycollic acid. The series of reactions above described may therefore be represented by the following equations:



ETHYLENE SELENIOCYANATE, $C^2H^4(CNSe)^2$, formed by digesting potassium seleniocyanate with ethylene bromide, crystallises from alcohol in white needles, insoluble in cold water and in ether, slightly soluble in hot water and in cold alcohol. By prolonged boiling with nitric acid, it is converted into ethylene-selenic acid, $C^2H^4(SeO^2H)^2$, which is very deliquescent, and yields a lead, a silver, and a barium salt (Proskauer).

ETHYLENE-THYMOL. See THYMOL.

ETHYL-EUGENOL. See EUGENOL.

ETHYL-GLYCERIN. G. Glinsky, in 1868, by treating monochloraldehyde

in aqueous solution with potassium cyanide, obtained an oily compound which he regarded as cyanaldehyde (*Zeitschr. f. Chem.* 1868, 617); subsequently, however (*ibid.* 1870, 441), he found that when treated with hydrochloric acid it yielded chlorolactic and acetic acids, and he then designated it as the *cyanochlorhydrin of ethyl-glycerin*, representing it by the constitutional formula $\text{OH}^{\cdot}\text{Cl}^{\cdot}\text{CH}^{\cdot}\text{OH}^{\cdot}\text{CO}^{\cdot}\text{CH}^{\cdot}\text{CN}^{\cdot}$. Butlerow (*Deut. Chem. Ges. Ber.* vi. 1256) regards it rather as an ethereal compound, $\text{OH}^{\cdot}\text{Cl}^{\cdot}\text{CH}^{\cdot}(\text{CN}^{\cdot})\text{O}^{\cdot}\text{CO}^{\cdot}\text{CH}^{\cdot}$.

ETHYL-GLYCOLLYL NITRIL, $\text{CH}^{\cdot}(\text{OC}^{\cdot}\text{H}^{\cdot})\text{CN}^{\cdot}$, is obtained by heating ethyl-glycollamide, $\text{CH}^{\cdot}(\text{OC}^{\cdot}\text{H}^{\cdot})\text{CO}^{\cdot}\text{NH}^{\cdot}$ with an equivalent quantity of phosphorus

135°. Like other nitrils, it combines with gaseous hydrobromic acid, forming a crystalline compound which is insoluble in ether, and resolved by water into its components. Aqueous acids or alkalis convert the nitril into ethylglycollic acid.

The same nitril is produced by distilling the amide with phosphorus pentachloride; the product contains a combination of the nitril with phosphorus trichloride. This body, which could not be obtained in a pure state, is a liquid, fuming in the air, and boiling at about 100°–105°. Henke obtained similar compounds of acetonitril and propionitril. The nitril of ethylglycollic acid is also formed, but mixed with secondary products, by distilling the amide with phosphorus pentasulphide (L. Henry, *Deut. Chem. Ges. Ber.* vi. 259).

ETHYL-GUANIDINE. See GUANIDINE.

ETHOXYLAMINE. See HYDROXYLAMINE.

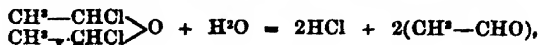
Bromide, $\text{CH}^{\cdot}-\text{CHBr}^{\cdot}$.—According to Tawildarow (*Liebig's Annalen*, clxxvi. 12) this compound is converted by ammonia, not into an ethylenamine (like ethylene bromide under similar circumstances), but like the chloride (*2nd Suppl.* 378), into collidine. The reaction takes place most readily at 125°–140°. Ethylidene bromide heated to 120°–140° with *potassium acetate* in alcoholic solution is converted into aldehyde, ethyl acetate, and acetal. An alcoholic solution of *potassium sulphhydrate* does not act upon ethylidene bromide, and may therefore be used to separate this compound from ethylene bromide.

Bromodioxethylidene, $\text{C}^{\cdot}\text{H}^{\cdot}\text{BrO}^{\cdot}=\text{C}^{\cdot}\text{H}^{\cdot}\text{Br}(\text{OH})^{\cdot}$.—This is the compound formed by the action of phosphorus pentabromide on aldehyde, and formerly regarded as an isomeric of ethylene bromide (i. 107). To prepare it, aldehyde is gradually poured upon well-cooled phosphorus pentabromide, and the reaction, which is at first very violent, is afterwards completed at a temperature of 60°. The resulting phosphorus oxybromide is decomposed by ice, and the oil which separates is washed with steam: it cannot be distilled alone without decomposition. The same compound is formed by heating aldehyde to 130° with acetyl bromide (Tawildarow, *loc. cit.*)

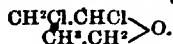
Ethylidene Chloride, $\text{CH}^{\cdot}-\text{CHCl}^{\cdot}$, is converted by the action of chlorine into monochlorethylidene chloride, $\text{CH}^{\cdot}\text{Cl}-\text{CHCl}^{\cdot}$, and dichlorethyl chloride, $\text{CH}^{\cdot}-\text{CCl}^{\cdot}$ (Staedel, *Deut. Chem. Ges. Ber.* vi. 1403).

Oxychloride, $\text{C}^{\cdot}\text{H}^{\cdot}\text{Cl}^{\cdot}\text{O}^{\cdot}$.—This compound, isomeric with dichlorinated ethyl oxide, is prepared by passing hydrochloric acid into well-cooled aldehyde till two layers of liquid are formed, the upper consisting chiefly of the oxychloride, the lower of strong aqueous hydrochloric acid. Instead, however, of immediately rectifying the upper layer over calcium chloride, as in Lieben's original process (ii. 509), whereby a large portion is charred and destroyed, it is better to heat this upper layer to 100° for about six hours in a stream of carbon dioxide, and then submit it to fractional distillation. By this means tolerably pure ethylidene oxychloride is obtained, boiling between 116° and 117° (F. Kessel, *Liebig's Annalen*, clxxv. 44).

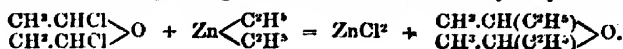
Ethylidene oxychloride treated with water splits up into hydrochloric acid and aldehyde, whence it appears to have the constitution $(\text{CH}^{\cdot}-\text{CHCl}^{\cdot})_2\text{O}^{\cdot}$:



the isomeric compound dichlorethyl oxide being represented by the formula,



That ethylidene oxychloride actually has the constitution above given is shown by its reaction with zinc-ethyl, the product of which is secondary butylic ether:



To prepare this butylic ether, the oxychloride is slowly added to zinc-ethyl diluted with common ether in an apparatus filled with carbon dioxide, due precautions being taken to prevent too great a rise of temperature: to complete the reaction, however, the heat of a water-bath must be applied. After distilling off the ethylic ether and fractionating, a product is obtained, boiling at 120° – 125° , but still containing chlorine, which may be removed by digestion with sodium. The product then boils constantly at 120° – 121° , has a sp. gr. of 0.750 at 21° , and agrees in every respect with the secondary butylic ether obtained from erythrite (Kessel).

Ethylidene Iodide, $\text{CH}^2\text{—CH}^2\text{I}^2$, is formed by dropping ethylidene chloride into a solution of aluminium iodide in carbon disulphide:



The product separated from the deposit, washed with water and rectified, yields the ethylidene iodide as a brownish liquid of sp. gr. 2.84, boiling with partial decomposition between 177° and 179° , sparingly soluble in alcohol, and probably identical with the body which Bertholot obtained by the action of hydriodic acid on acetylene (1st Suppl. 34). Heated on the water-bath with a dilute alcoholic solution of potash, it is resolved into alcohol and vinyl iodide, $\text{C}^2\text{H}^2\text{I}$, identical with that which is prepared from ethylene iodide (Gustavson, *Deut. Chem. Ges. Ber.* vii. 731).

ETHYLIDENE-DIBENZAMIDE, $\text{C}^{10}\text{H}^{10}\text{N}^2\text{O}^2 = \text{CH}^2.\text{CH}(\text{NH}.\text{CO}.\text{C}^6\text{H}^5)^2$. This compound, which Limpricht obtained in 1856 by the action of aldehyde-ammonia on benzoyl chloride (i. 567), is also produced: α . By dissolving benzamide in aldehyde to which a few drops of hydrochloric acid have been added. The reaction is attended with rise of temperature, and the solution on cooling deposits the compound in the form of a white crystalline mass (Nencki, *Deut. Chem. Ges. Ber.* vii. 158). β . By gradually adding benzonitril (2 mols.) with agitation, to well-cooled strong sulphuric acid containing 1 mol. paraldehyde, leaving the liquid to itself for a few hours, and then adding water, whereupon the compound separates as a white powder, which may be washed with ammonia and recrystallised from alcohol (Hepp a. Spiess, *ibid.* ix. 1424).

Ethylidene-dibenzamide dissolves easily in chloroform, carbon sulphide, ether, and hot alcohol, but is nearly insoluble in water. From the alcoholic solution it crystallises on cooling in long white needles which melt at 204° (Hepp a. Spiess) at 188° (Nencki) and sublime at a higher temperature. Heated with alcoholic potash-solution, it yields benzoic acid, and when boiled with mineral acids it takes up water and is resolved into aldehyde and benzamide.

Trichlorethylidene-dibenzamide, $\text{CCl}^3.\text{CH}(\text{NH}.\text{CO}.\text{C}^6\text{H}^5)^2$, prepared in like manner from benzonitril and chloral, crystallises from boiling alcohol in wavelitic groups of needles melting at 257° , and decomposing at a higher temperature. It dissolves sparingly in ether, more easily in chloroform and carbon sulphide, and reacts with acids and with alcoholic potash like ethylidene-dibenzamide (Hepp a. Spiess).

Similar compounds are obtained from benzonitril and *bromal*, *butyl-chloral* and *valeraldehyde*. Benzonitril and benzaldehyde do not act on one another under similar conditions. The compound which Hübner a. Schreiber obtained by the action of chloral on acetonitril (p. 439) has probably also a similar constitution, viz. that of *trichlorethylidene-diacetamide*, $\text{CCl}^3.\text{CH}(\text{NH}.\text{CO}.\text{CH}^3)^2$: (Hepp a. Spiess.)

ETHYLIDENE-GLYCOLLIC ETHER, or *Monethylic Ethylidenate*, $\text{CH}^2.\text{CH} \begin{smallmatrix} \text{OH} \\ \text{OC}^2\text{H}_5 \end{smallmatrix}$ is formed, together with formic acid, ethyl acetate, aldehyde, and acetal, by the action of electrolytic oxygen on ethyl alcohol. It is a liquid which dissolves sparingly in water, boils between 88° and 90° , and is oxidised by chromic acid to acetic acid (A. Renard, *Compt. rend.* lxxx. 105).

ETHYL-MALONIC ACID, $\text{CH}^2.\text{CH}^2.\text{CH}(\text{CO}^2\text{H})^2$. See MALONIC ACID.

ETHYL-METHYL-CARBONYL OXIDE and **SULPHIDE**. See BUTYL ETHERS (p. 359).

ETHYL-METHYL-SULPHINE-COMPOUNDS. See SULPHINES.

ETHYL-NAPHTHENOXAMIDE. See NAPHTHALENE-COMPOUNDS.

ETHYL-NITROLIC ACID. See NITROLIC ACID.

See OXAMIC ETHERS.

See OXAMIDE.

ETHYL-OXYBENZOIC ACID, $\text{C}^7\text{H}^5(\text{C}^2\text{H}^5)\text{O}^2$. On the characters of this acid, as prepared from ethyl-metacresolate, see p. 582.

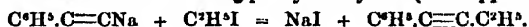
ETHYL-OXYBUTYRIC ACIDS, $\text{CH}_3\text{CHOH}.\text{CH}(\text{C}^2\text{H}_5).\text{CO}^2\text{H}$. See BUTYRIC ACIDS, OXY- (pp. 364-365).

ETHYL-OXYOXYALYL CHLORIDE, $\text{COCl}-\text{CO}(\text{OC}^2\text{H}_5)$. This compound, produced by the action of phosphorus oxychloride on ethyl oxalate (2nd Suppl. 883) is strongly attacked by zinc-ethyl. On adding 2 mols. of the latter by drops to 1 mol. of the chloride contained in a well-cooled vessel, the mass gradually becomes darker-coloured and more viscid, and finally pitchy, and a combustible gas, probably ethane, is given off; on treating the product with water, more ethane is evolved and zinc hydroxide is produced. If the whole be then distilled, and the distillate dried with potassium carbonate and rectified, a colourless mobile liquid is obtained, tasting and smelling like peppermint; very sparingly soluble in water. Sp. gr. = 0.98 at 12° : b. p. = 175° – 176° : vapour-density = 5.36. This product is ethylic diethyl-glycolate, $\text{C}(\text{C}^2\text{H}_5)_2(\text{OH})-\text{CO}.\text{OC}^2\text{H}_5$, identical with the ethylic leucate or diethoxalate described by Frankland & Duppa (iv. 273). Hence it appears that, under the conditions in which the chlorides $\text{C}^2\text{H}_5\text{COCl}$ yield ketones, the chloride of ethyloxalic acid yields the corresponding tertiary alcohol (L. Henry, *Deut. Chem. Ges. Ber.* v. 949).

ETHYL-OXYSULPHOBENZIDE. See OXYSULPHOBENZIDE.

ETHYL-PHENOL. See PHENOLS.

ETHYL-PHENYL-ACETYLENE, $\text{C}^{10}\text{H}^{10} = (\text{C}^6\text{H}_5)\text{C}\equiv\text{C}(\text{C}^2\text{H}_5)$ (T. M. Morgan, *Chem. Soc. Jour.* 1876, i. 162). This compound is formed by the action of ethyl iodide on the sodium-derivative of phenyl-acetylene (1st Suppl. 5):



The two substances, in equivalent proportions, mixed with a quantity of anhydrous ether sufficient to give fluidity to the mass, are heated in sealed tubes to 120° – 140° , whereupon a brisk reaction takes place, and a large quantity of combustible gas is formed, so that it is advisable to open the tubes from time to time in order to relieve the pressure. On filtering the liquid product from the sodium iodide and distilling, ethyl-phenyl-acetylene passes over at 200° , and a small quantity of resinous matter is left behind.

Ethyl-phenyl-acetylene, after being purified by two or three distillations, is a colourless, very refractive liquid, having a peculiar odour, a sp. gr. of 0.923 at 21° , and boiling at 201° – 203° . It unites directly with bromine, and, when heated with fuming hydrobromic acid yields a hydrobromide heavier than water, smelling like peppermint, and partly decomposed by distillation.

The hydrobromide, heated to 150° – 160° in sealed tubes with glacial acetic acid and an equivalent quantity of silver acetate, yields the corresponding acetate, $\text{C}^{10}\text{H}^{10}\left\{\begin{smallmatrix} \text{H} \\ \text{OC}^2\text{H}_3\text{O} \end{smallmatrix}\right.$, a fragrant liquid, boiling at 223° – 230° , and convertible, by digestion over the water-bath with caustic potash, into the alcohol $\text{C}^{10}\text{H}^{10}\left\{\begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}\right.$.

This alcohol, when purified by several distillations, is a colourless liquid, having a pleasant odour, a sp. gr. of 0.986 at 19° , boiling at 224° – 226° , and combining readily with bromine. Its constitution might be represented by either of the following formulæ:



but further experiments are required to show which of these is the true one.

ETHYL-PHENYL-CARBAMIDES. See CARBAMIDES (p. 391).

ETHYL-PHENYL KETONE. See PHENYL KETONES.

ETHYL-PHENYL-OXAMIDE. See OXAMIDE.

ETHYL-PHENYL-SEMICARBAZIDE. See HYDRAZINE-COMPOUNDS.

ETHYL-PHLORETIC ACID. See PHLORETIC ACID.

ETHYL-PHOSPHINE. See PHOSPHINES.

ETHYL-PROPYL CARBINOL. See HEXYL ALCOHOLS.

ETHYL-PROPYL KETONE. See PROPYL KETONES.

ETHYL-PYROGALLOL. See PYROGALLOL.

ETHYL-PYRROL, $\text{C}^2\text{H}(\text{C}^2\text{H}_5)\text{N}$. This compound is produced by distillation of neutral ethylammonium mucate, $\text{C}^2\text{H}^5\text{O}(\text{C}^2\text{H}_5.\text{NH}_2)^2$. Mucic acid dissolves rapidly

in a solution of ethylamine, with considerable rise of temperature. The solution, when evaporated, deposits rhombic prisms of ethylammonium mucate, which closely resemble those of the ammonium salt, but are distinguished therefrom by their great solubility in alcohol. The salt decomposes when distilled, evolving carbon dioxide. The distillate separates into two layers, the lower of which consists of a solution of ethylammonium carbonate, and the upper of ethyl-pyrrol, which is a liquid boiling at 131° , and having the smell and external characters of ordinary pyrrol. Its sp. gr. at 16° is 0.8881 (C. A. Bell, *Deut. Chem. Ges. Ber.* ix. 935).

ETHYL-SUCCINIMIDE. See SUCCINIMIDE.

ETHYL-SUCCINURIC AMIDE, $C^4H^4O^2 \begin{smallmatrix} \text{NH}^2 \\ \text{NH} \end{smallmatrix} \text{CO-NH}(C^2H^5)$, is formed by the action of alcoholic or aqueous ammonia on the compound of succinimide and ethyl cyanate, $(C^4H^4O^2)HN.CN(C^2H^5)O$ (succidecyanic ether), produced by direct combination of the two. It crystallises in needles, melts at 199° , and is decomposed by heating with aqueous ammonia (Menschutkin, *Deut. Chem. Ges. Ber.* vii. 128).

ETHYL-SULPHACETIC ACID, $C^2H^5.S.CH^2.COOH$.

ETHYL-SULPHINACETIC ACID, $C^2H^5.SO.CH^2.COOH$. } See SULPH-ACETIC ACIDS.

ETHYL-SULPHONACETIC ACID, $C^2H^5.SO^2.CH^2.COOH$. }

ETHYL-SULPHINIC ACID, $C^2H^5.SO^2H$. } See SULPHUROUS ETHERS.

ETHYL-SULPHONIC ACID, $C^2H^5.SO^3H$. }

ETHYL-SULPHURIC CHLORIDE. See SULPHURYL CHLORIDE.

ETHYL-TERPENE. See TERPENES.

ETHYL-THRENE. See METHYL-THRENE.

ETHYL-THIOCARBIMIDE, $CS=N-C^2H^5$, is easily produced by the action of ethylamine on thiocarbonyl chloride:



(Ruthke, *Liebig's Annalen*, clxvii. 211).

ETHYL-THIOSULPHURIC ACID, $C^2H^5.S^2O^2H$. See THIOSULPHURIC ACID under SULPHUR, OXYGEN-ACIDS OF.

ETHYL-TOLUENE, $C^9H^{12} = C^6H^4(CH^3)(C^2H^5)$. Meta-ethyl-toluene, $C^6CH^3.H.C^2H^5.H^2$, is prepared by boiling an ethereal solution of ethyl bromide and meta-bromotoluene (2nd Suppl. 1164) with sodium for two days. This product, finally rectified over sodium, is a colourless liquid boiling at 158° – 159° , and having a sp. gr. of 0.869 at 20° . By oxidation with chromic acid, it yields isophthalic acid. With sulphuric acid it forms two meta-ethyl-toluenesulphonic acids. The barium salt of the α -acid, $(C^6H^4SO^3)^2Ba + 6H^2O$, forms large well-defined crystals, sparingly soluble in water; the barium salt of the β -acid is easily soluble and crystallises in small prisms (Wroblewsky, *Deut. Chem. Ges. Ber.* vii. 140).

Para-ethyl-toluene, $C^6.CH^3.H.H.C^2H^5.H^2$, is prepared by the action of sodium on a mixture (not exceeding 28 to 30 grams) of para-bromo-toluene and ethyl iodide. The product, after repeated rectification, boils at 161° – 162° , and does not solidify in a freezing mixture. By oxidation with nitric acid it yields pure paratoluic acid.

Nitro-ethyltoluenes.—Para-ethyltoluene, treated at ordinary temperatures with fuming nitric acid, yields two isomeric dinitro-ethyltoluenes, $C^9H^{10}(NO^2)^2$, one of which separates from the oily product, on standing over sulphuric acid, in limpid monoclinic prisms or large tables, whilst the other forms an oil which does not solidify even in a freezing mixture. The solid modification dissolves easily in hot, less easily in cold alcohol, and separates therefrom by slow crystallisation in very large crystals having a rhombohedral character and melting at 52° . Both these dinitro-compounds, when further treated with a mixture of nitric and sulphuric acids yield one and the same trinitro-para-ethyltoluene, $C^9H^7(NO^2)^3$, in crystals unaccompanied in either case by an oil. This trinitro-compound melts at 92° , dissolves sparingly in cold, much more freely in boiling alcohol, and crystallises therefrom in stellate groups of short, hard prisms (Jannasch & Dieckmann, *Deut. Chem. Ges. Ber.* vii. 1613).

ETHYL-VANILLIN. See VANILLIN (p. 305).

ETHYL-VINYL, $C^4H^5 = CH^2-CH^2-CH=CH^2$. *Normal Butylene* (p. 357).—Lieben (*Bull. Soc. Chim.* [2], xii. 282) obtained ethyl-vinyl acetate by trans formation of secondary butyl iodide, prepared by the action of HI on butylene chlorhydrin, $C^4H^9(OH)Cl$ (1st Suppl. 375). This acetate boils at 105° – 111° , and has a

sp. gr. of 0.896 at 0°. Heated with excess of strong aqueous potash in sealed tubes for ten hours to 130°–135°, it yields secondary butyl alcohol, $\text{CH}_3\text{—CH}_2\text{—CHOH—CH}_3$, boiling at 98.5°–99°, and having a sp. gr. of 0.834 at 0°, and 0.818 at 21° (Nevold, *Compt. rend.* lxxv. 514; compare Chapman, 1st *Suppl.* 377).

Ethyl-vinyl bromide, $\text{CH}_3\text{—CH}_2\text{—CHBr—CH}_2\text{Br}$ (b. p. 164°–165°) is formed, together with ethylene bromide (b. p. below 130°) and monobromethylene bromide (above 180°) by heating 2 pts. vinyl bromide and 1 pt. zinc-ethyl in sealed tubes for five or six weeks. The ethyl-vinyl bromide, heated with silver acetate and acetic acid in sealed tubes, yielded a distillate which, when freed from silver by baryta and from baryta by carbonic acid, formed a thick, colourless, sweet liquid, boiling at 192°–193°, and having the composition of butylene glycol, mixed with a little ordinary glycol. The butylene glycol thus prepared is identical with that which Grabowsky a. Saytzeff obtained by saponifying normal butylene bromide with potash or baryta (p. 362).

ETTRINGITE. This mineral occurs in association with chalcocorphite (a calcio-aluminic silicate described by G. vom Rath, *Pogg. Ann. Ergänzungsband*, vi. 376), from which it can scarcely be distinguished in external appearance. It is hexagonal, exhibiting the forms P , ∞P , OP , $\frac{1}{2}P$. Axial ratio $a : c = 1 : 0.9434$. Angle $P : \infty P = 137^\circ 27'$ (measured); $P : P$ in the terminal edge = $136^\circ 46'$, in the lateral edge = 94.64° ; inclination of the face P to the vertical = $42^\circ 33'$; inclination of the terminal edge P to the vertical = $46^\circ 40'$. Sp. gr. = 1.7504. Hardness a little less than that of gypsum. Cleavage prismatic, perfect. Swells up before the blowpipe, but does not fuse. Soluble in hydrochloric acid, and for the greater part in water; the aqueous solution is strongly alkaline. The crystals give off water even at 100°, and acquire a silky lustre; at 120° they give off 33 per cent. water; at 150°, 34 per cent.; at 200°, 36 per cent.; and at a red heat, 45.8 per cent. Quantitative analysis gave:

Al_2O_3	SO_3	CaO	H_2O
7.76	16.64	27.27	45.82 .. 97.49

The determination of the sulphuric acid was attended with loss, so that this constituent should perhaps be estimated 2.51 per cent. higher. With this allowance, the analysis agrees nearly with the formula $\text{Al}_2\text{O}_3.3\text{SO}_3 + 6(\text{CaO.H}_2\text{O}) + 26\text{aq.}$, which requires 8.21 per cent. Al_2O_3 , 19.12 SO_3 , 26.77 CaO , and 45.90 H_2O (Lehmann, *Jahrb. f. Min.* 1874, 273).

EUCALYPTUS. According to Faust a. Homeyer (*Deut. Chem. Ges. Ber.* vii. 63, 1429), the oil of *Eucalyptus globulus* contains a terpene boiling at 150°–151°, another terpene called eucalyptene, boiling at 172°–175°, together with cymene and a camphor-like body, $\text{C}^{10}\text{H}^{16}\text{O}$. The terpene boiling at 150°–151° is present in small quantity only; it takes fire with iodine, and resinifies on exposure to the air.

The oil called eucalyptol by Cloez (2nd *Suppl.* 493) is a mixture of about 70 per cent. eucalyptene and 30 per cent. cymene. After rectification over sodium, it boils between 171° and 174°. It dissolves in all proportions in absolute alcohol, ether, and chloroform, and in about 15 pts. of 90 per cent. alcohol; has the odour of a fine terpene; detonates with iodine; absorbs oxygen with avidity; turns brown with strong sulphuric acid; and is converted by oxidation with dilute nitric acid into paratoluic and terephthalic acids.

The eucalyptene and cymene contained in eucalyptol cannot be separated by fractional distillation. To obtain the cymene, the mixture was shaken with sulphuric acid diluted with one-fourth part of water, and then heated, whereby the eucalyptene was polymerised; then, after three days, the liquid was mixed with water and distilled, whereby a distillate was obtained, consisting of cymene, which, after repeated rectification over sodium, boiled at 173°–174°. The barium salt of the cymenesulphonic acid prepared from it had the composition $(\text{C}^{10}\text{H}^{16}\text{SO}_3)_2\text{Ba} + 3\text{H}_2\text{O}$, and the properties described by Heilstein a. Kupfer (2nd *Suppl.* 420).

The camphoroidal body, $\text{C}^{10}\text{H}^{16}\text{O}$, is a colourless oily liquid which becomes faintly yellowish on exposure to light, boils at 216°–218°, is insoluble in aqueous potash, and yields cymene when distilled with phosphorus pentasulphide. Its analysis gave numbers intermediate between those required by the formulae $\text{C}^{10}\text{H}^{16}\text{O}$ and $\text{C}^{10}\text{H}^{14}\text{O}$, but the reactions of the body show that it is not an oxycymene (Faust a. Homeyer).

Oppenheim a. Pfaff (*Deut. Chem. Ges. Ber.* vii. 626) have examined Australian eucalyptus oil, probably obtained from *Eucalyptus odorata* and *E. amygdalina*. By repeated treatment with potash, washing with water, and fractionation, it yielded eucalyptene, $\text{C}^{10}\text{H}^{14}$, boiling at 172°–175°, and having a vapour-density = 68.56 and 68.22 (calc. 68, $\text{H} = 1$). This hydrocarbon did not form a crystallised compound with hydrochloric acid, or yield a crystallised hydrate when left for six months in contact with nitric acid and alcohol. When treated with half the calculated quantity

of iodine, it was converted into cymene, $C^{10}H^{14}$, which, when oxidised with dilute nitric acid, yielded paratoluic acid melting at 173° – 175° . The crude oil did not yield any oxidised compound answering to the eucalyptol of Cloes.

By exhausting old leaves of *Eucalyptus globulus* with alcohol, a complex resin is obtained consisting of tannin; a resinous acid dissolving with crimson colour in sulphuric acid; a new fatty acid melting at 245° – 247° , and containing 77 per cent. carbon and 11 per cent. hydrogen; an alcohol which is perhaps ceryl alcohol; and several resins (P. A. Hartzler, *Deut. Chem. Ges. Ber.* ix. 314).

This name is given by Shepard to a variety of magnesia mica, found at Chester, Massachusetts, in schistose masses formed of scales having an easy cleavage parallel to the base. Translucent in thin plates. With the polarising microscope it exhibits a single negative axis across the base. Colour deep green. Somewhat flexible. Hardness 2.5. Density 2.84. Composition:—

SiO^2	Al^2O^2	Fe^2O^2	MgO	Alkalis	Loss on ignition
39.55	15.95	7.80	22.25	10.35	4.10

(Pisani, *Compt. rend.* lxxxiii. 166).

EUGENOL, $C^{10}H^{12}O^2 = C^4H^3(OH)(OCH^3)(C^3H^5)$ (Church, *Chem. Soc. J.* 1875, 113; Wassermann, *Liebig's Annalen*, clxxix. 366). Pure eugenol prepared, as already described (ii. 604), by treating oil of cloves with aqueous potash, acidulating the alkaline liquid with hydrochloric acid, and distilling, has a specific gravity of 1.066 at 15° (Church), 1.0788 at 0° , 1.0630 at 18.5° (Wassermann), and boils at 244° (uncorr.), 251.8 (corr.) (Church), at 246° (Wassermann). It does not reduce alkaline cupric solutions even at the boiling heat, but reduces ammoniacal silver-solutions when left in contact with them, even at ordinary temperatures. By chromic acid mixture it is quantitatively oxidised to carbon dioxide, acetic acid, and water (Wassermann). When distilled with caustic baryta, the greater part of it is carbonised, but a small portion is converted into a compound having the composition of methyl-eugenol, $C^{11}H^{14}O^2$, but differing from that substance by its boiling point, which is 262.5° (corr.), whereas methyl-eugenol boils at 237° – 239° (Church).

When bromine is added to an ethereal solution of eugenol, as long as any action takes place, and the ether then evaporated, a brown viscous residue is left which shows no tendency to crystallise, but is probably an addition-product, similar to that which is obtained in like manner from ethyl-eugenol, *infra* (Wassermann).

Constitution of Eugenol.—This compound is intimately related to coniferol, $C^9H^{10}(OCH^3)$, potash, methyl-protocate, the oxidation of its potassium salt with potassium permanganate (p. 305). Acetyl-eugenol, formed by heating eugenol with acetic anhydride, yields by oxidation with permanganate a mixture of acetovanillic acid and acetovanillin, which, when treated with a solution of sodium hyposulphite, are converted respectively into vanillic acid and vanillin. Now in all these compounds the hydroxyl-group stands in the para-position, and the methoxyl-group in the meta-position, with respect to the third lateral chain, viz. C^4H^3OH in coniferol, $COOH$ in vanillic acid, COH in vanillin: hence, also, in eugenol the relative positions of the lateral chains must be:

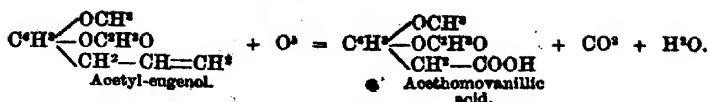


Substitution-derivatives of Eugenol.

Acetyl-eugenol, $C^{11}H^{14}O^2 = C^4H^3(OCH^3)(OC^2H^3O)(C^3H^5)$, is prepared by boiling a mixture of equal parts of eugenol and acetic anhydride for three or four hours in a vessel with a reflux condenser. On distilling the product, acetic acid and anhydride pass over first, and then the thermometer rises quickly to 270° , at which temperature the acetyl-eugenol distils over as a colourless oil, which solidifies on cooling to a crystalline mass.

Acetyl-eugenol melts at 30° – 31° , dissolves easily in alcohol and ether, is insoluble in water and in cold dilute alkalis, and is decomposed by boiling caustic alkalis into eugenol and acetic acid. Strong sulphuric acid dissolves it with deep red colour.

Acetyl-eugenol is oxidised by potassium permanganate solution at 35° – 40° , to acetovanillic acid, $C^{10}H^{10}O^4$, and acet- α -phahomovanillic acid, $C^{11}H^{12}O^4$ (see HOMOVANILIC ACID). The formation of this last acid shows that the radicle C^4H^3 in eugenol has the constitution of allyl $—CH^2—CH=CH^2$.



The acetovanillic acid, which is the sole product obtained at higher temperatures, results from oxidation of the remaining group CH^2 (Tiemann & Nagajosi-Nagai, *Deut. Chem. Ges. Ber.* x. 202); see also Erlenmeyer (*ibid.* 628).

The derivatives of eugenol containing ethyl and its homologues are prepared by heating potassium-eugenol with the iodides or bromides of the various radicles, and a little alcohol in sealed tubes.

Ethyl-eugenol, $\text{C}^{12}\text{H}^{14}\text{O}^2 = \text{C}^6\text{H}^3(\text{OCH}^3)(\text{OC}^2\text{H}^5)(\text{C}^2\text{H}^5)$. Wassermann (*Liebig's Annalen*, clxxix. 366) prepares this compound by gradually dropping ethyl bromide (33 parts) into a mixture of 50 eugenol, 17 potassium hydroxide, and 40 water, heated in the water-bath in a vessel fitted with a vertical condensing tube kept cool by ice. The heating is continued till the smell of ethyl bromide is no longer perceptible, the liquid then diluted with water, and the ethyl-eugenol thereby separated is further treated with potash and with water, and dried over calcium chloride.

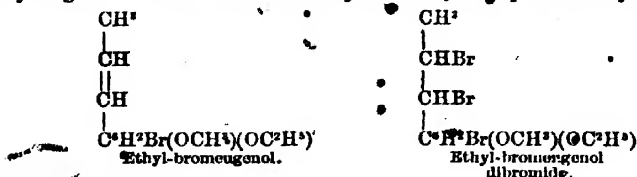
Ethyl-eugenol boils at 260° (under 713 mm.), or at 254° (under 760); has a density of 1.0280 at 0° , and 1.0117 at 18.5° ; does not act on vegetable colours. When distilled it partly polymerises, and at 258° a brownish resinous mass is left behind; and by washing this mass with water and crystallising it from alcohol, laminae are obtained having the composition of ethyl-eugenol, melting at 125° and subliming at a higher temperature.

Ethyl-eugenol, oxidised by chromic acid mixture, yields acetic and ethyl-methyl protocatechuic acids:



together with acetaldehyde and a small quantity of a crystalline body which smells like vanilla and melts under water (Wassermann).

Action of Bromine on Ethyl-eugenol.—When ethyl-eugenol is treated with bromine in the manner above described with respect to eugenol itself, a crystalline mass is obtained which, after being purified by crystallisation from hot alcohol, has the composition $\text{C}^{12}\text{H}^{13}\text{BrO}^2$. It forms lustrous silky needles which melt at 80° , and may be sublimed unchanged. It is readily soluble in ether. When this compound, which may be regarded as an addition-product of monobromothyleugenol, $\text{C}^{12}\text{H}^{13}\text{BrO}^2$, is treated in alcoholic solution with metallic zinc, the additive bromine is removed, and a colourless compound obtained, crystallising in large rhombic prisms which melt at 48° . This is soluble in alcohol and ether, and possesses a blue and rose fluorescence. Its composition is represented by the formula $\text{C}^{12}\text{H}^{14}\text{BrO}^2$, and as neither silver acetate nor potassium acetate or ethylate has any action on it, it is almost certain that the bromine-substitution has taken place in the benzene-nucleus and not in the side chain. The substituted bromine may therefore be most conveniently displaced from the compound $\text{C}^{12}\text{H}^{13}\text{BrO}^2$ by means of nascent hydrogen, treating it in alcoholic solution with sodium-amalgam: the product thereby obtained is ethyl-eugenol. The two bromine-compounds may be represented by the formulæ



(Wassermann, *loc. cit.*)

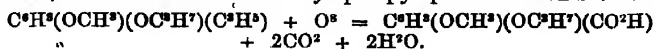
The higher homologues of ethyl-eugenol have been prepared and examined by Cahours (*lxxxiv.* 151). They are all converted by gradual oxidation into homologues of protocatechuic acid.

Propyleugenol, $\text{C}^{14}\text{H}^{16}\text{O}^2 = \text{C}^6\text{H}^3 \begin{array}{c} \text{OCH}^3\text{CH}^2\text{CH}^3 \\ \text{OCH}^3 \\ \text{C}^6\text{H}^3 \end{array}$, is obtained by heating in a

flask, subsequently sealed in the blowpipe, a mixture of 100 parts of eugenol, 100 parts of propyl iodide, and 34 or 35 parts of potassium hydrate, previously dissolved in strong alcohol. The mixture, which must be shaken from time to time, deposits potassium iodide, after which the flask is heated for some hours in a water-bath, until the deposition of potassium iodide ceases, whereupon the heat is withdrawn and the con-

tents of the flask are treated with water. A heavy oil then separates, which is washed with potash and water, dried with calcium chloride, and finally distilled, the portion passing over between 260° and 270° being collected apart.

Propyl-eugenol is a mobile liquid, of a light amber colour, with an odour resembling cloves. It is insoluble in water, but dissolves easily in alcohol and in ether. Its density is 1.0024 at 16°; it boils between 263° and 265°. Bromine and fuming nitric acid attack it violently. By gradual oxidation with a hot dilute solution of potassium permanganate, it is converted into methyl-propyl-protocatechuic acid:



Isopropyl-eugenol, $\text{C}^{13}\text{H}^{18}\text{O}^2 = \text{C}^6\text{H}^3[\text{CH}(\text{CH}^3)_2](\text{OCH}^3)(\text{C}^3\text{H}^3)$, obtained like the preceding compound, boils between 252° and 254°, and has a density of 0.199 at 17°.

Butyl-eugenol, $\text{C}^{14}\text{H}^{20}\text{O}^2 = \text{C}^6\text{H}^3(\text{OC}^4\text{H}^9)(\text{OCH}^3)(\text{C}^3\text{H}^3)$, prepared in like manner with butyl iodide, is a faint amber-coloured liquid boiling between 272° and 274°, and having a density of 0.985 at 15°. Potassium permanganate oxidises it to methylbutyl-protocatechuic acid, $\text{C}^{12}\text{H}^{18}\text{O}^4 = \text{C}^6\text{H}^3(\text{OCH}^3)(\text{OC}^4\text{H}^9)(\text{CO}^2\text{H})$.

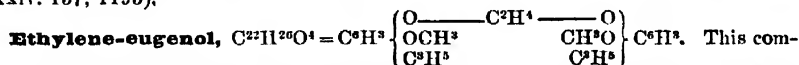
Amyl-eugenol, $\text{C}^{15}\text{H}^{22}\text{O}^2 = \text{C}^6\text{H}^3(\text{OC}^5\text{H}^{11})(\text{OCH}^3)(\text{C}^3\text{H}^3)$, closely resembles the preceding compounds. It boils between 283° and 285°; has a density of 0.976 at 16°, and is insoluble in water, but soluble in alcohol and ether. Its odour resembles, at the same time, that of cloves, and that of the amyl-compounds. Potassium permanganate, at a temperature of 75°–80°, oxidises it to amyl-methyl-protocatechuic acid, $\text{C}^{13}\text{H}^{18}\text{O}^4 = \text{C}^6\text{H}^3(\text{OC}^5\text{H}^{11})(\text{OCH}^3)(\text{CO}^2\text{H})$.

Hexyl-eugenol, obtained by the action of hexyl chloride on potassium-eugenol, is an amber-coloured liquid, boiling between 296° and 300°.

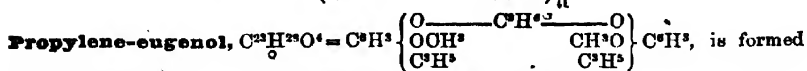
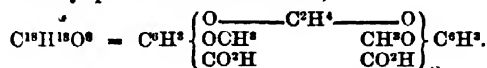
Allyl-eugenol is obtained by the action of allyl bromide on potassium-eugenol. On distilling the product, a portion passes over between 267° and 270°, then the temperature rises to 300°, and the liquid which passes over solidifies on cooling into a resinous mass. The first product gave numbers leading to the formula $\text{C}^{11}\text{H}^{16}\text{O}^2$, and is, therefore, allyl-eugenol, $\text{C}^6\text{H}^3(\text{OC}^3\text{H}^5)(\text{OCH}^3)(\text{C}^3\text{H}^3)$. The second body gave the same numbers, and is, therefore, a polymeride: it boils between 284° and 290°.

Benzyl-eugenol is prepared in the same way as the preceding compounds, and resembles them in every respect. It is partially decomposed by distillation.

Eugenols containing Diatomic Alcohol-radicles (Cahours, *Compt. rend.* lxxxiv. 157, 1195).



pound, formed by the union of 2 mols. of eugenol having their hydroxylic hydrogen-atoms replaced by the bivalent radicle C^2H^4 , which joins them together, is prepared by heating in a sealed tube a mixture of eugenol, alcoholic potash, and ethylene bromide. When purified in the usual way, it appears as a mass of splendid white plates, with nacreous reflections. It is insoluble in water and cold alcohol, but dissolves in hot alcohol, which deposits it again on cooling in large nacreous plates, melting at 89°. Ether, benzene, toluene, glacial acetic acid, and acetic ether dissolve it on heating, and deposit it on cooling in well-defined crystals. Nitric acid and bromine attack it violently. Phosphorus pentachloride at a gentle heat attacks it strongly, forming a brownish-yellow resin, insoluble in water, slightly soluble in alcohol and ether. By potassium permanganate, ethylene-eugenol is oxidised to ethylene-di-methylprotocatechuic acid,



by heating trimethylene dibromide for some hours in a sealed tube placed in a water-bath with an equivalent proportion of potassium-eugenol and a little alcohol. An abundant deposit of potassium-bromide is then formed, and the liquid on cooling becomes filled with splendid crystals of propylene-eugenol, which, when washed with potash and water, dried between blotting-paper, and dissolved in boiling alcohol, separates out in nearly colourless crystals, and after recrystallisation from ether,

forms colourless, satiny crystals closely resembling ethylene-eugenol. From alcohol it separates in small, shining, colourless prisms. Potassium permanganate oxidises it to propylene-di-methylprotocatechuic acid, $C^{10}H^{12}O^4$.

A compound isomeric with the propylene-eugenol just described is obtained by heating propylene dibromide, $CH^2-CHBr-CH^2Br$, with potassium-eugenol and alcohol. On evaporating the alcoholic liquid separated from the potassium bromide, and washing the residue with potash and water, a heavy aromatic oil remains, which deposits a few crystals; and on pressing these between bibulous paper and recrystallising from ether, needle-shaped crystals are obtained having the composition $C^{22}H^{20}O^4$, and melting at $56^\circ-58^\circ$ (Cahours).

A bismuth silicate hitherto known only as occurring at Schneeberg in Saxony (ii. 606), has lately been found also at Johanngeorgenstadt. The Schneeberg mineral, however, occurs in distinguishable crystalline forms of clove-brown colour, whereas that from Johanngeorgenstadt forms transparent, colourless, or wine-yellow spherules resolvable by the lens into groups of perfectly rounded crystals. These spherules gave by analysis 16.67 per cent. silica, and 81.82 bismuth oxide, together with 0.90 ferric phosphate, agreeing with the formula $2Bi_2O^3 \cdot 3SiO^2$ (16.25 silica and 83.75 bismuth oxide), which is that of the Schneeberg mineral as determined by G. vom Rath. The spherules are implanted on quartz, and accompanied by bismuth, bismuth ochre, and cloanthite. Eulytin is often accompanied by an arsenite of bismuth called *agricolite* (p. 48). (Frenzel, *Jahrb. f. Mineralogie*, 1873, 785).

EUPHORBIA. The ash of *Euphorbia amygdaloides* has been analysed by Wittstein (*Arch. Pharm.* [3], iv. 341), with the following results:

1. On siliceous soil. Total ash of air-dried plant = 5.936 per cent.

K ² O	Na ² O	Na (with Cl)	CaO	MgO	AlPO ³	Fe ² O ³
33.441	1.443	1.155	15.121	4.371	1.057	0.419
Mn ² O ³	Cl	SO ³	PO ³	SiO ²	CO ²	
0.344	1.781	7.135	5.414	12.093	15.832	

2. From another siliceous soil. Total ash = 4.850 per cent.

K ² O	Na ² O	Na (with Cl)	CaO	MgO	AlPO ³	Fe ² O ³
15.362	0.298	0.540	33.135	4.796	1.325	0.656
Mn ² O ³	Cl	SO ³	PO ³	SiO ²	CO ²	
trace	0.836	3.733	4.474	8.684	25.970	

According to P. H. Dilg (*Pharm. J. Trans.* [3], vii. 455), the aqueous extract of the root of *Euphorbia Ipecacuanha* does not contain sugar, but gives the sugar reaction after boiling with hydrochloric acid. The alcoholic extract contains fat, a waxy substance, and a crystalline body. The extract prepared with petroleum-ether contains euphorbone (1st Suppl. 609).

1. Of the Bat.—W. M'Murtrie (*American Chemist*, iv. 339) has analysed the excrements of the common bat found in a cave about two miles long, in which these animals collect in large numbers. The layer of excrement is in many parts 15 feet thick. Its analysis gave:

Moisture	12.8000
Organic matter	9.7000
Silica, insoluble in hydrochloric acid	42.2900
soluble	9.4100
phosphoric acid (P ² O ³) sol. in water	0.2277
" " " insol. "	1.4673
" " oxide "	0.1169
Alumina	19.8890
Lime	1.6377
Magnesia	2.6900
Nitric acid	0.0823
Sulphuric acid	
Soda	traces
Carbonic acid	

99.7019

See also Pppp (2nd Suppl. 496).

2. Of Poultry.—Experiments have been made by W. von Knieriem (*Zeitschr. f. Biologie*, xiii. 36), with the view of determining the effect produced on the excrements

of birds by substances, such as asparagine, aspartic acid, glycocine, leucine, and ammonium salts, which are known to be converted into urea in the bodies of mammals. The result has been to show that, in the bodies of poultry all these substances are converted into uric acid, with the exception of the ammonium salts, which leave the body of the fowl in their original state. This accounts for an excess of ammonia in the excrement beyond that necessary to combine with the uric acid present. During the digestion of proteids by fowls, the same bodies are formed as in the case of ammonia, viz. aspartic acid, leucine, and glycocine, and these products may be regarded as the forerunners of uric acid.

EXPLOSION. The following statement of the composition of various explosive materials of recent introduction is given by A. Nobel (*Monit. Scientif.* vi. 248). The proportions of material used in the manufacture of dynamite are: strong nitric acid 1.15 pts.; strong sulphuric acid 2.00; glycerin 1.45, and 0.25 dry infusorial silica. Explosives of similar composition are: ammonia-powder, dualin, seranim and lithofracteur. Ammonia-powder is prepared with 80 pts. ammonium nitrate, 6 wood-charcoal, and 16-20 pts. nitroglycerin. It excels dynamite in explosive power, but the ammonium nitrate renders it hygroscopic. Seranim is a mixture of potassium chlorate and nitroglycerin: the chlorate enhances the price and the dangerous character of the product, without improving it. Dualin is a mixture of saw-dust, saltpetre and nitroglycerin: it has not come into use. Lithofracteur consists, according to the statements of the manufacturers, of 55 nitroglycerin, 21 infusorial silica, 6 wood-charcoal, 15 barium nitrate mixed with neutral sodium carbonate, and 3 sulphur with manganese dioxide. Dynamite 'No. 2' is ordinary gunpowder having its sulphur replaced by nitroglycerin.

The following are the relative ballistic powers of these compounds, that of nitroglycerin being = 100:

	For equal Weight	For equal Volumes
Compressed gun-cotton	71	45 ⁴
Dynamite (0.25 silica, 0.75 nitroglycerin)	72	74
Ammonia-powder	83	80
Comp. gunpowder mixed with 20 per cent. nitroglycerin	50	—
Strongly explosive powder of Curtis, a. Harvey	28	17.5
Mercuric fulminate	30	—
The strongest lithofracteur	56.5	53

Roux a. Sarrau (*Compt. rend.* lxxix. 757) have determined the different forces exerted by various explosive substances, according as the substance is made simply to deflagrate (explosion of the second order), or to detonate by the percussion of mercuric fulminate (explosion of the first order). The reciprocals of the weights (after due corrections) of each substance, which, when exploded in the two ways just mentioned, sufficed to rend similar cast-iron shells, gave the relative explosive forces. Some of the results are given in the following table, the explosive force of gunpowder ignited in the ordinary manner being taken as 100:

	Explosive force	
	1st Order	2nd Order
Mercury fulminate	928	—
Gunpowder	434	100
Nitroglycerin	1013	480
Gun-cotton	646	300
Picric acid	550	204
Potassium picrate	531	182
Barium picrate	550	171
Strontium picrate	451	135
Lead picrate	594	146

Roux a. Sarrau (*ibid.* lxxvii. 138, 478) have also determined the heat of combustion of various explosive substances. The experiments were made with cylindrical cast-iron shells, having a thickness of metal equal to 6 mm., and an internal capacity of 270 to 280 c.c. The powder was exploded by means of a wire ignited by an electric current. The shell was immersed in a copper vessel containing water, the temperature of which was observed before and after the explosion. The results are given in the following table:

	Composition of Powder			Heat-units evolved for 1 kilo. of powder	Weight of gases per kilo. of powder
	Nitre	Sulphur	Charcoal		
Sporting powder . . .	78	10	12	307.3	0.357
Ordnance powder . . .	75	12.5	12.5	752.9	0.412
Rifle powder . . .	74	10.5	15.5	730.8	0.414
Blasting powder . . .	62	20	18	570.2	0.499

In another set of experiments the volume of gas produced by the combustion of the several kinds of powder was determined by exploding the powder in a wrought-iron cylinder of known capacity connected with a mercurial pressure-gauge.

The results obtained are tabulated as follows :—

	Heat-units. (kil.-degrees)	Degrees C. (absolute temperature)	Vol. of gas in litres reduced to 0° and 760	Pressure in atmospheres	
Sporting powder	807.3	4654	234		373
Ordnance powder	752.9	4360	261	4168	349
Rifle powder .	730.8*	4231	280	4339	339
Blasting powder	570.2	3372	307	3792	270

Experiments were also made with dynamite, gun-cotton, and other explosive mixtures with the following results :

	Heat-units	Weight of gas for 1 kgr.	Vol. of gas for 1 kgr.
Gun-cotton	1056.3	0.853	720 litres
Dynamite of 75 per cent.	1290.0	0.600	455 "
Picrate of potassium	787.1	0.740	576 "
Mixture of 55 parts picrate and 45 } nitrate of potassium	916.3	0.485*	334 "
Mixture of equal parts of picrate and } chlorate of potassium	1180.2	0.466	329 "

Igniting Temperature of Explosive Bodies.—When explosive substances are slowly warmed, they detonate at a lower temperature than when they are suddenly heated. To eliminate this source of error in the determination of the temperature of ignition, F. Hess (*Dingl. pol. J.* ccxviii. 227) introduced into the bath in which a substance had been exploded by gradual heating, a second sample of the same substance at the temperature of the explosion, and repeated this treatment till the times during which the samples had to remain in the bath before explosion were found to be equal in two successive experiments. The mean of the two temperatures thus observed was taken as the temperature of ignition. By this method it was found that the purest gun-cotton, prepared by Lenk's process, exploded at 260°; dynamite prepared with infusorial silica at 230°; Schultze's powder at 220.75°. This method, however, requires considerable time, and an approximate estimate of the temperature may be obtained as follows: A sheet of thick platinum foil, horizontally extended, is heated near the end by a blow-pipe flame, and the places on the sheet at which, with a given power of flame, cadmium, tin, bismuth, lead, antimony, &c., enter into fusion are marked. By this means, the kindling temperatures of the explosives may be compared with the melting points of the several metals.

On the influence of this cause on the Explosion of Compressed Gun-cotton, see Champion & Pellet (*Compt. rend.* lxxxi. 962; *Chem. Soc. Jour.* 1876, i. 516). The same authors direct attention to certain analogies between the phenomena of explosion and those of the sudden crystallisation of salts from their supersaturated solutions (*Compt. rend.* lxxvii. 53; *Chem. Soc. Jour.* 1873, 1103).

Explosions in Flour-mills.—These explosions may be due either to the rapid combustion of finely divided flour diffused through the air, or to the ignition of a mixture of air with gases produced by the decomposition of flour.

a. When flour is mixed with air, and a candle is brought in contact with the mixture, it will ignite and fire off, just like a mixture of air and inflammable gas. If the stones of a flour-mill are placed too close together, they occasionally strike, producing sparks, which ignite a small portion of the cloud of fine particles surrounding the apparatus, the motion of the elevator promoting the combustion by creating a current of air. The combustion, thus favoured, passes instantly through the whole room, and an explosion follows.

b. Flour and bran, intimately mixed give off at 450° C., a gas which, when mixed with 9 vols. of air, forms an explosive mixture easily ignited by a spark from the stones of the mill. (See *Dingl. pol. J. chem.* 417; *Chem. Soc. Jour.* 1873, 420.)

Explosions in Hydrogen Generators.—These explosions may be prevented by attaching to the exit-end of the apparatus, and therefore after the wash-bottle, a small tube containing discs of wire-gauze pressed between cotton-wool (Fresenius, *Zeitschr. anal. Chem.* 1873, 73).

EXTRACTS. A method for the preparation of extracts without heat is described by A. Herrera (*Pharm. J. Trans.* [3], viii. 283). He finds that on congealing the solutions of vegetable juices, and in general of aqueous solutions of organic principles, the dissolved principles remain in the mother-liquors, and that two or three congelations are generally sufficient to produce a solution concentrated enough to allow of the extracts being finished either by exposure to the sun, or in the drying-closet. The congelation is performed in a freezing-machine (sorbetière), with a freezing-mixture of ice and either water or calcic chloride. After a large portion of the solution has congealed, the ice-mass is pressed, and the mother-liquor congealed a sufficient number of times, just short of the precipitation of any sparingly soluble principles. Extracts so prepared are said to represent accurately the properties of the plants, which is not always the case with those which are obtained by heat-concentration. Conium extract, for example, when thus prepared, has the characteristic odour of conine, and when dissolved in water resembles the juice of the plant in appearance and properties, its albumin being unaltered.

On the quantities of Extract obtainable from various Vegetable Substances, see Drukworth (*Arch. Pharm.* [3], vi. 128; *Jahresb. f. Chem.* 1875, 821).

F

FAMATINITE. See ENARGITE (p. 733).

FASSAITE. On Fassaita from the lava of Santorin, see Fouqué (*Compt. rend.* lxxx. 631; *Chem. Soc. Jour.* 1875, 624). On Pseudomorphs of Fassaita after Monticellite, see G. vom Rath (*Jahrb. Min.* 1874, 413; *Jahresb. f. Chem.* 1874, 1289).

FAT. *Formation in the Animal Body.*—Experiments have been made by Weiske a. Wildt (*Zeitschr. f. Biologie*, x. 1) to determine whether the formation of fat in animals is due to the carbohydrates or to the proteids of the food. Of four male pigs six weeks old, fed and treated in the same manner, two were killed, and used for estimation of fat, nitrogenous tissue, and mineral substance; the third was fed with food poor in albumin, and the fourth with food rich in albumin; the last, however, did not long sustain this diet, and must therefore be excluded from the results of the experiment. The pig which was fed for 184 days on food poor in albumin (starch, bran, potatoes) digested the non-nitrogenous substance (starch) almost completely, the proteids to the amount of three-fourths, of the fat only one-fourth. At the conclusion of the feeding experiment, the amount of fat, proteids, and mineral substance were determined in the slaughtered animal. The carcasses of the sucking pigs contained large quantities of water with only small amounts of fat, whereas, in the pig fed on potatoes, this proportion was reversed. A comparison of the composition of the sucking pigs, of the pig fed as above, and of the food given to it, showed that, with a diet poor in albumin, the proteid substance was sufficient to account for all the flesh and fat produced.

On the preparation of Emulsions of solid Fats, see Mattison (*Pharm. J. Trans.* [3], iv. 998).

On the determination of the specific gravity of Fats, see G. W. Wiggner (*Analyst*, i. 146; and C. Eatcourt, *Chem. News*, xxxiv. 254).

On the estimation of Fat in Milk, see MILK.

Decomposition of Fats.—A method of decomposing fats, devised by J. C. Bock of Copenhagen, is described by W. Lant Carpenter (*Chem. News*, xxvi. 88). Bock found, by microscopical examination, that neutral fat consists of small spherules surrounded by albuminous envelopes, the removal of which is the first step in the decomposition of the fat. This is effected in Bock's process by leaving the fat for some time in contact with strong sulphuric acid, and the neutral fat thus released from its envelope is in a condition to be easily decomposed by boiling with water. The fatty acids thus separated are brown, but may be bleached by the action of oxidising substances, then washed with water, and subjected to cold and warm pressing. Tallow, treated in this manner, yields, according to Bock (*Dingl. pol. J.* cxviii. 230), 95 per cent. of fatty acids and 6.66 per cent. of glycerin, but about 2 per cent. of the fatty acids is lost during the oxidation and washing.

On some peculiar modifications of Animal Fats, resulting from the Fermentation and Digestion of the Neutral Fats of Food prior to and during Assimilation, see H. C. Bartlett (*Analyst*, i. 175; *Chem. Soc. Jour.* 1877, ii. 207).

Black or dark brown feathers or hair, treated successively with alcoholic ammonia and with dilute sulphuric acid, yield a black residue, containing, according to the mean of ten analyses of feathers from several species of *Corvus*, 55.4 per cent. carbon, 4.25 hydrogen, and 8.5 nitrogen, a composition which may be represented by the empirical formula $C^8H^8NO^4$. This black pigment is not altered by dilute acids or alkalis, but is oxidised by nitric acid. Bromine acts upon it, forming several compounds, one of which is soluble in water, and gives a characteristic spectrum. The solutions obtained by treating the feathers with dilute sulphuric acid also gives very decided absorption-spectra. The feathers of the common rook contain about 1 per cent. of the black pigment (Hodgkinson & Sorby, *Pharm. J. Trans.* [3], vii. 432; *Chem. Soc. Jour.* 1877, i. 426).

On the Dyeing of Feathers, see *Dingl. pol. J.* cxviii. 318; cexi. 1069; *Chem. Soc. Jour.* 1873, 1069; 1874, 1193; also *Chem. Centr.* 1872, 743; *Chem. Soc. Jour.* 1873, 423.

FEHLING'S COPPER-SOLUTION. According to Boivin & Loiseau (*Compt. rend.* lxxix. 1263), this solution, when diluted with distilled water, deposits cupric oxide on boiling, and becomes more or less decolorised, but the decoloration does not take place when the liquid is diluted with river (Seine) water, the salts in which appear to prevent the decomposition which is produced by the action of the water alone. G. Missaghi (*Gazz. chim. ital.* 1875, 414) thinks it preferable to add to the liquid a few drops of a solution of tartaric acid or Rochelle salt.

According to P. Lagrange (*Compt. rend.* lxxix. 1005), a very stable solution, not reduced either by boiling or by addition of cane-sugar, is obtained by dissolving 10 pts. of pure cupric tartrate in 500 pts. of distilled water and 400 pts. of caustic soda, and keeping the solution at the boiling heat for twenty-four hours, renewing the water as it evaporates. The cupric tartrate is prepared either by decomposing cupric sulphate with neutral sodic tartrate, or by dissolving recently precipitated and well-washed cupric hydroxide in the requisite quantity of sodium tartrate. Missaghi observes that in whatever way the solution may be prepared, the only way of preserving it unaltered is to enclose it in sealed tubes and keep it in the dark.

FELSITE. Analyses of the Felsite-rocks of Queensland, have been made by R. Daintree (*Geol. Soc. Qu. J.* xxviii. 271; *Jahresh. f. Chem.* 1873, 1216, 1216).

Microscopical examinations of Saxon Felsites and Pitchstones have been published by E. Kalkowsky (*Jahrb. f. Min.* 1874, 646).

FELSPAR. *Artificial Formation.*—Hautefeuille (*Compt. rend.* lxxxv. 1043) has lately succeeded in producing crystals of orthoclase and albite by heating the elements of these minerals in presence of certain fused salts, such as tungstic acid or alkaline tungstates: thus a mixture of silica and alumina in presence of acid potassium tungstate, at a temperature between 900° and 1000°, produces tridymite, orthoclase, and triclinic feldspars. If the potash and alumina are in the proper proportions, the tridymite and triclinic feldspars disappear after 15 to 20 days' heating, and the orthoclase alone remains. A highly alkaline silicoaluminate of potassium containing 1 mol. AlO^3 to 6 mols. SiO^2 mixed with tungstic acid gives the same result. When soda is substituted for potash, other conditions remaining the same, albite is formed.

natural ones, are not attacked by acids. The crystallographic examination of the artificial albite shows that it almost exactly resembles the natural crystals from Dauphiné and Tyrol. The crystals having the composition of orthoclase appear

to be analogous to those found in the St. Gothard. The specific gravities of the crystals of these minerals, natural and artificial, are as follows:

	Natural	Artificial
Orthoclase	2.4-2.62	2.55
Albite	2.59-2.65	2.61

Crystals of orthoclase have been found accidentally produced in the upper parts of copper-smelting furnaces at Sangershausen in the Mansfeld, and at Stolberg in the Harz.

Monoclinic Felspars. C. Bischof (*Dingl. pol. J.* cxvii. 319) has analysed a number of felspars of the orthoclase type from a newly discovered stratum in the gneiss of the Odenwald. In the following table the felspars are arranged in the order of their fusibility, which is the same as that of their acidity, the most fusible and most acid being placed first:

SiO ²	Al ² O ³	Fe ² O ³	CaO	MgO	K ² O	Na ² O	Loss on ignition
67.92	18.90	1.28	2.02	0.39	1.87	6.93	0.61 = 99.92
65.61	18.04	0.88	0.31	—	10.65	0.49	— = 100.01
64.44	18.75	0.65	0.27	—	13.82	2.40	— = 100.33
64.40	18.91	0.67	0.24	—	13.76	2.17	— = 100.15
64.26	17.79	1.73	0.23	—	14.44	1.77	— = 100.22

Bischof also gives formulae for calculating the relative fusibility from the chemical composition; see *Chem. Soc. J.* 1876, i. 527; 1877, i. 446.

The Sodium Felspar of Pantellaria. (H. Förstner, *Jahrb. f. Min.* 1877, 942). The greater part of the trachytic rocks of the island of Pantellaria are characterised by the presence of an unusually large amount of soda, pointing to the presence of a sodium felspar. Two varieties of this sodium felspar occur, differing from each other crystallographically and chemically; they are—

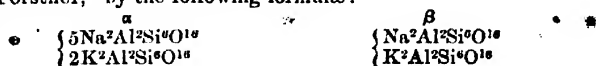
a. Sodium Felspar from Cuddia Mida.—This is found in the vitreous lava of the crater of Cuddia Mida in tabular crystals (through $\infty R\infty$), exhibiting the usual twin forms peculiar to orthoclase. Sp. gr. 2.55.

SiO ²	Fe ² O ³	Al ² O ³	CaO	MgO	Na ² O	K ² O
66.63	0.72	19.76	0.38	0.30	7.31	4.86 = 99.96

b. Sodium Felspar from Monte Gibele.—Occurs in an andesitic rock in long prismatic crystals, th. tabular type through $\infty R\infty$ being rare. Sp. gr. 2.61.

SiO ²	Fe ² O ³	Al ² O ³	CaO	MgO	Na ² O	K ² O
63.41	3.27	20.32	2.76	0.30	7.42	2.53 = 100.01

The two minerals differ but slightly in composition, that from Cuddia Mida having, however, a higher percentage of soda. The analytical results may be represented, according to Förstner,* by the following formulae:



These minerals are therefore monoclinic felspars having the composition of albite, and containing only a secondary amount of the isomorphous potassium compound. The existence of such orthoclases is a proof of the dimorphism of the compound $\text{Na}^2\text{Al}^2\text{Si}^4\text{O}^{18}$, whilst the dimorphism of the corresponding potassium compound has been proved by the discovery of microcline by Descloizeaux (p. 775). Groth observed that the dimorphic modifications of potash felspar (potash-orthoclase and microcline) exhibit an extraordinary closeness in their angular measurements, and it now appears, from Förstner's examinations of the sodium-felspars of Pantellaria, that a similar coincidence is observed in their angular measurements with those of the other dimorphic modifications of albite.

Triclinic felspars. Descloizeaux (*Compt. rend.* lxxx. 364; *Jahrb. f. Min.*

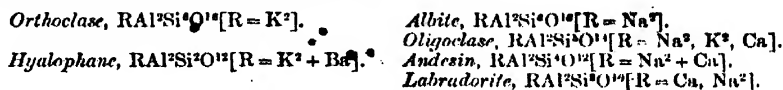
mineral species, and not, as supposed by Tschermak and vom Rath, isomorphous mixtures of albite and anorthite (*2nd Suppl.* 510). *Albite* and *oligoclase* are distinguished from one another by the position of the planes of their optic axes. *Labradorite* exhibits constant optical characters, and is distinguished by a strong dispersion, $\rho > \nu$, round the positive bisectrix, and cannot therefore be regarded as a mixture of

* The formula β , however, requires a greater percentage of potash than of soda, whereas the analysis gives less.

albite, which has a positive bisectrix and dispersion $\rho < \nu$, and anorthite, which has a similar dispersion and a negative bisectrix. Senarmont's observations on the two varieties of Rochelle salt have shown indeed that the optical properties of a mixed salt are variable, and approach most nearly to those of the predominating constituent. *Oligoclase* appears also to be a distinct species, the orientation, both of its positive and of its negative bisectrix, being constant in all cases. *Andesin* appears, from the examination of somewhat imperfect specimens, to exhibit the same optical properties as oligoclase.

With regard to the chemical constitution of these felspars, Descloizeaux draws attention to the view suggested by Friedel and other chemists, that the several species of triclinic felspar differ from one another only in their proportions of silica, forming in fact a series whose common difference is 1SiO_2 , thus:—Anorthite + $\text{SiO}_2 = \text{Labradorite}$; Labradorite + $\text{SiO}_2 = \text{Andesin}$; Andesin + $\text{SiO}_2 = \text{Oligoclase}$ (which will accordingly exhibit the oxygen-ratio 1 : 3 : 10, agreeing with many analyses); and, finally, Oligoclase + $\text{SiO}_2 = \text{Albite}$. Descloizeaux considers that the composition of the triclinic felspars may be equally well represented either by this view or by the mixture-theory of Tschermak, but that the former accords best with the optical and crystallographic characters of the several species.

Petersen (*Jahrb. f. Min.* 1874, 269) also regards andesin, oligoclase, and labradorite as distinct mineral species, and not as mixtures of albite and anorthite. He represents the known species of felspar by the following formulæ:



Vom Rath, on the other hand, is of opinion that the chemical constitution of the triclinic felspars is most satisfactorily represented by the mixture-theory. In support of this view he adduces some analyses which he has recently made of plagioclases from volcanic rocks, selected with great care with regard to their purity. The results are given in the following table, the last column of which shows the proportion of albite and anorthite molecules, which in isomorphous mixture would produce a felspar having a composition similar to that determined by the analysis.* The calculated composition of such a mixture is shown by the black figures below.

	Potash			Soda	Molecules of albite and anorthite
Antisana, Plagioclase crystal from a spherulitic lava.	64.27	22.30	3.12	2.11	7.30 5 + 2,
	64.12	22.62	3.52		9.74
Perlenhardt in Transylvania, from Drachenfels-trachyte	62.18	23.52	5.33		8.97* 3 + 2 }
	61.91	24.11	5.22		8.73
Conejos, Rio Grande, Colorado, from obsidian-like andesite	61.88	24.18	4.79	2.50	
Toluca, Mexico, from andesite	59.79	24.43	7.41	0.64	7.24
	59.73	25.59	6.97		7.71
Tunguragua, Ecuador, from andesite	57.8	25.75	9.05		6.04* 3 + 4 }
	58.00	26.76	8.33		6.92
Palma, Canary Islands, from basyn-trachyte	55.64	28.89	10.92	0.71	5.08 1 + 2
	55.43	28.49	10.95		5.73 Labradorite

Considering now that these plagioclases were not freely developed in drusy cavities, but had separated from the ground-mass (sometimes in granules scarcely a millimeter in size), that consequently the crystals could not have been perfectly pure, and taking into account the numerous difficulties of the analysis, vom Rath regards the preceding table as affording a very satisfactory confirmation of Tschermak's conclusion, deduced from more than 100 careful analyses, that the formation of plagioclases by the mixture of albite and anorthite substance is an established fact, and not a mere mode of explanation.

* Determined by loss.

successive addition of silica-molecules takes no account of the replacement of lime and soda, which is so intimately related to the variation of the amount of silica. This fundamental fact, the increase of lime with decrease of silica, and the increase of silica with increase of soda, is, however, the very basis of Tschermak's theory.

Vom Rath likewise discusses other objections which have been raised against Tschermak's theory. (1.) To a suggestion of Descloizeaux, that the deviations from a simple ratio of the oxygen in the silica to that in the bases may be attributed to foreign minerals enclosed in the felspar crystals, he replies that it may be asked why the proportion of $(\text{CaO} + \text{Na}_2\text{O}) : \text{Al}_2\text{O}_3 = 1 : 3$ is not likewise disturbed by the presence of such imbedded minerals. In this case also the theory of Tschermak affords the real solution of the difficulty.* (2.) The view formerly entertained by Ch. Deville and others, that andesin is merely an altered oligoclase, is refuted by numerous analyses of well-defined specimens of andesin from various localities. (3.) Fouqué has suggested that the constancy of the ratio $1 : 3$ of $(\text{Na}_2\text{O} + \text{CaO})$ to Al_2O_3 in the plagioclases may be attributed to the fact that many of the analyses of supposed pure material have really been made on mixtures of triclinic felspars, existing together in the same rock in microscopic crystals, and very difficult to separate. To this vom Rath replies, that though such mixtures may often exist, such was not the case with the plagioclases above considered—the analyses of which were made on microscopic crystals of uniform aspect throughout—or on the splendid crystals obtained from Vesuvius.

On the Optical Characters of Orthoclase and of Triclinic Felspars, see Descloizeaux (*Compt. rend.* lxxxii. 1017; *Chem. Soc. J.* 1876, ii. 611).

On Twin-formation in Triclinic Felspars, see G. vom Rath (*Jahrb. f. Min.* 1876, 689; *Jahresh. f. Chem.* 1876, 1236).

On the Constitution of Triclinic Felspars, see further Petersen (*Jahrb. f. Min.* 1874, 269; *Chem. Soc. J.* 1874, 877).

Vom Rath has also published the following analyses of felspars from various localities (*Zeitschr. geol. Ges.* xxvii. 295; *Jahrb. f. Min.* 1874, 310; *Pogg. Ann.* clii. 39).

1. Felspar from the augitic syenite of the Piano del Monzoni. The analysis leads to the formula $\text{Or}^4\text{Ab}^1\text{An}^1$.* 2. Orthoclase rich in sodium from the augitic syenite of the Pyrenees. 3. Felspar, $\text{An}^{12}\text{An}^3\text{Ab}^3$, from the augitic labrador-rock of the Piano del Monzoni. 4. Felspar, from the diabase of Monte Monzoni. The analysis is referred to the formula An^2Ab^1 , and the differences are attributed to the numerous microscopic crystals enclosed in the felspar. 5. Labradorite, An^2Ab^1 , from the gabbro of Monte Monzoni. 6. Light, flesh-coloured, somewhat decomposed anorthite, from the same locality on Monte Monzoni, from which are derived monticellite (*q.v.*) and its pseudomorphoses. 7. White, much decomposed anorthite from the same locality. 8. A labradorite, an analysis of which has been already given (*2nd Suppl.* 512, analysis *g* in table), but occurring, not in porphyrite as formerly stated, but in basalt.

Nos. 9 to 12 are analyses of triclinic felspars from rocks collected by Wolf in Ecuador. 9 is from a quartz-andesite from the volcano of Mojanda or Yana-Urcu, between Perucho and Puéllaro. In a light-reddish ground-mass are enclosed quartz, a small quantity of mica, and magnetic iron oxide, together with crystals of triclinic felspar measuring 5 mm. From the crater of Pululagua. The reddish rock contains a small quantity of mica, together with triclinic felspar crystals measuring from 2 to 3 mm.: the cavities appear to contain tridymite. 11. From Guagua-Pichincha. The obsidian-like rock encloses small triclinic felspars, hornblende, olivine (?), augite, mica, and a large quantity of magnetic iron oxide. 12. This felspar has the composition of a normal andesin, to which the three preceding felspars may also be referred. 13 is a labradorite, An^2Ab^1 , from the hornblende-andesite of Pomasqui, near Quito.

* Or. = orthoclase; Ab. = albite; An. = anorthite.

	SiO ^a	Al ^a O ^a	FeO	MgO	CaO	K ^a O	Na ^a O	Total (%)	Loss by ignition	Sp. gr.
1.	63.45	19.81	—	—	1.51	12.34	2.47	= 99.58	0.57	2.536
2.	64.86	18.78	—	—	—	9.23	5.37	= 98.24	0.04	2.549
3.	61.81	30.55	—	0.10	12.08	2.63	2.85	= 99.82	0.56	2.707
4.	55.83	27.57	1.29	—	7.03	3.56	4.09	= 99.37	1.36	2.690
5.	55.51	28.99	—	—	8.41	2.51	4.48	= 100.90	0.49	2.868
6.	41.18	35.55	—	—	19.65	—	undet.	= 99.15	—	—
7.	40.17	33.51	—	—	21.56	—	undet.	= 99.90	4.66	—
8.	55.24	28.32	—	—	10.63	—	5.81(?)	= 100	0.65	2.711
9.	60.48	25.35	—	—	7.25	0.08	7.28	= 100.44	0.04	2.666
10.	59.39	26.08	—	—	8.20	0.22	6.7*	= 100.63	0.12	2.659
11.	59.1	26.1	—	—	8.8	0.5	5.5	= 100	1.01	2.620
12.	59.73	25.59	—	—	6.97	—	7.71	= 100	—	—
13.	55.86	28.10	—	—	10.95	—	5.09(?)	= 100	0.11	2.644

(*) For Nos. 1-5 and 8-13 the totals are reckoned exclusively, for Nos. 6 and 7 inclusively of the loss by ignition.

(*) a. *) Determined by difference.

Albite. Crystals of albite from the Schneeberg near Passau, are described by J. Rumpf (*Jahrb. f. Min.* 1874, 865). They are implanted on magnetic pyrites, have a light to dark olive-green colour, and all agree in having the process of the brachy-pinacoid and of the macrodomes very largely developed. The simplest combination is $\infty P \infty . \infty P \infty . 0P$; another, of frequent occurrence is $\infty P \infty . P \infty . 0P \infty . P$. Optical examination shows that the crystals are free from twin-formation. Sp. gr. = 2.61. Analysis (1) below.

Analyses. (2). Albite from Kragerø (vom Rath, *Jahrb. f. Min.* 1870, 689). (3). Decomposed soda-felspar from Bare-hills, Maryland (Leeds, *Amer. Chemist*, 1873, iv. 164). (4). Albite from Media, Delaware County, Pennsylvania, with delicate striation and moonstone shimmer on the cleavage-faces (Leeds, *Sill. Am. J.* [3], vi. 25). (5). A very large crystal (4.5 centimeters by 3.5 and 1.5) from Guatemala; exhibiting, according to a closely approximate measurement, the new prismatic face $\infty P \frac{2}{3}$ (A. v. Lasaulx, *Jahrb. f. Min.* 1875, 147). (6 and 7). Perthite-like aggregations between albite and orthoclase from veins in the granulite field of Saxony (Crodner, *Zeitschr. geol. Ges.* xxvii. 104). Analysis by Schwarz: (6). Rochsburg, from a pegmatite vein. (7). Burgstadt, from a granite vein.

	SiO ^a	Al ^a O ^a	Fe ^a O ^a	MgO	CaO	Na ^a O	K ^a O	Total (%)	Loss by ignition	Sp. gr.
(1.)	66.13	20.93	2.24	0.64	—	11.10	—	= 101.04	—	—
(2.)	66.30	20.90	—	0.35	—	12.10	—	= 100	0.35	—
(3.)	66.86	20.30	—	1.41	0.23	10.57	—	= 100.14	0.77	—
(4.)	67.70	19.98	trace	1.47	0.11	8.86	1.36	= 99.56	0.08	—
(5.)	68.79	19.34	—	—	—	9.26	2.29	= 100	0.32	—
(6.)	64.65	19.63	—	0.30	trace	2.05	14.15	= 100.78	—	—
(7.)	66.88	19.61	—	0.44	—	4.00	9.95	= 100.88	—	—

In No. 6, the ratio of orthoclase to albite is 56 : 13; in No 8, it is 27 : 17.

Andesin. This felspar is found, accompanying corundum (p. 369) in the Cullukane mine, North Carolina. (1). Snow-white or bluish-white, striated; distinctly cleavable; occurs mixed with hornblende, but free from corundum. Sp. gr. = 2.611. Analysed by König. (2). Fine grained; probably formed from corundum. Sp. gr. = 2.610. Analysed by Chatard (F. A. Genth, *J. pr. Chem.* [2], ix. 49).

The two following felspars, analysed by Petersen (*Jahrb. f. Min.* 1874, 269), also agree with the formula of andesin. (3). Triclinic felspar from the coarse-grained

and magnesia, 0.20 per cent. lime and 0.40 per cent. silica, which may be approximately attributed to small quantities of adhering titanite iron and augite. (4). Tabular composite crystals, several centimeters long, of triclinic felspar (formerly mistaken for sanidin) occurring in the basalt of the Steinbühl, near Weilburg; transparent, colourless, with vitreous lustre and conchoidal fracture. Sp. gr. = 2.604.

	SiO ^a	TiO ^a	Al ^a O ^a	Fe ^a O ^a	MgO	CaO	Na ^a O	Total (%)	Loss by ignition	Sp. gr.
1.	57.29	—	26.52	0.21	0.15	7.80	6.75	= 100.48	1.43	—
2.	58.41	—	25.93	0.38	0.18	5.82	6.45	= 100.20	0.93	—
3 a.	58.77	0.28	26.30	0.31	0.18	6.90	6.67	= 99.01	trace	—
b.	59.79	—	25.91	—	—	6.86	6.83	= 100	—	—
4.	58.88	—	26.94	—	trace	7.06	6.01	= 100.47	—	—

For other analyses of Andesin, see table at the top of this page.

Oligoclase, occurs at Unionville, Pennsylvania, in yellowish and brownish-white granules, enclosing corundum and another mineral, probably spinel. It seldom exhibits distinct cleavage, but when it does, the cleavage-faces are striated (Genth, *J. pr. Chem.* [2], ix. 49).

SiO ²	Al ² O ³	Fe ² O ³	MgO	CaO	Na ² O	K ² O	Loss on ignition
59.35	24.16	0.61	0.34	3.08	7.22	3.78	1.96 = 100.50

For other analyses of Oligoclase, see table (p. 771).

Tschermakite. This name is given by v. Kobell (*J. pr. Chem.* [2], viii. 411), to a triclinic feldspar, occurring at Bamle in Norway, associated with Kjernfins. It is massive, cleavable in two directions inclined at 91°, and exhibits fine striations on the more distinct cleavage-face. Lustre vitreous. Colour greyish-white. Semi-transparent. Exhibits white phosphorescence when heated. Fuses to a translucent glass. Unattacked by acids until boiled, and then but slightly. Gives off a little moisture when heated. Hardness = 6. Sp. gr. = 2.64. Analysis gave—

SiO ²	Al ² O ³	MgO	Na ² O	H ² O
66.57	15.80	8.00	6.80	2.70 = 99.87

According to this analysis the magnesia appears to be an essential constituent. On the other hand, G. W. Hawes (*Sill. Am. J.* [2], vii. 479) has analysed the same mineral, and finds in it only a small amount of magnesia. His analysis,

SiO ²	Al ² O ³	Fe ² O ³	MgO	CaO	Na ² O	K ² O	Loss on ignition
66.04	20.33	0.20	1.11	1.29	10.01	0.21	0.95 = 100.23

gives the oxygen-ratio RO : R²O³ : SiO² = 1 : 2.8 : 10, which is approximately that of oligoclase (1 : 3 : 9).

Labradorite. A mineral from a Greenland rock, analysed by Janovsky (*Deut. Chem. Ges. Ber.* 1873, 145), was found to contain

SiO ²	Al ² O ³	Fe ² O ³	CaO	MgO	Na ² O	K ² O	Loss by ignition
57.63	24.32	3.92	7.65	0.68	2.41	4.03	0.12 = 100.76

This gives the oxygen-ratio RO : R²O³ : SiO² = 1 : 3 : 7, which is that of labradorite; but the ratio of K : Na is 2 : 1, whereas in labradorite it is 1 : 1.

Labradorite from the rock called *Iserite* (q.v.) has been analysed by G. Bertels (*Jahresb. f. Chem.* 1874, 1253) with the following results: A. Analysis. B. Calculated values for albite : anorthite = 1 : 4.

	SiO ²	Al ² O ³	Fe ² O ³	CaO	MgO	Na ² O
A.	53.51	29.37	trace	12.78	1.54	3.10 = 100.30
B.	51.2	31.3	--	13.6	---	3.7 = 99.8

On the other hand, the sp. gr. of the mineral, which is 2.668 at 4°, indicates rather the proportion albite : anorthite = 2 : 1.

With regard to this analysis, Tschermak remarks (*Jahrb. f. Min.* 1875, 313; *Min. Mittheilungen*, 1875, 41) that the crystalline forms of the plagioclases imbedded in trachytes and andesites can seldom be made out in the fresh rock, on account of their intimate union with the ground-mass, but that the pseudomorphs produced by weathering may often be easily separated and used for studying the forms. He has applied such pseudomorphous substances to the investigation of the forms of the labradorite of Verespatak in Transylvania. The microscopical examination of these pseudomorphs showed the presence of a mineral in their scales and laminae resembling kaolin, but not identical with it, also potash-mica in considerable quantity, a smaller quantity of plagioclase (undecomposed labradorite), quartz, a mineral occurring in veins which proved to be pennine, and finally brown iron ore.

The following is an analysis (A) by L. Sipocz, of the pseudomorphous mass compared with that of the unaltered labradorite (B).

	SiO ²	Al ² O ³	Fe ² O ³	CaO	MgO	Na ² O	K ² O	H ² O
A. 55.96	31.34	1.16	0.65	1.73	0.18	4.96	5.41	= 101.39
B. 55.21	28.56	1.00	10.76	0.53	4.37	—	—	= 100.43

Supposing the potash-mica to have the formula 2K²O.3Al²O³.6SiO².2H²O, the composition of the aluminium silicate will be Al²O³.4SiO² + H²O, which is that of pyrophyllite, and the mixture will consist of 44.76 per cent. pyrophyllite, 42.24 potash-mica, 4.51 pennine, 4.77 undecomposed labradorite, 3.12 quartz, and 1.35 brown iron ore.

A plagioclase, occurring in an andesite-lava from a great lava-stream between Riobamba and the Tunguragua in Ecuador, has been analysed by G. vom Rath (*Pogg. Ann. Ergänzungsband*, vi. 378). The feldspar crystals, 4 mm. long and 1 mm. thick,

are found imbedded in a blackish ground-mass, together with hornblende and finely divided magnetic iron oxide. Augite and olivine are altogether absent. The analytical numbers (mean of two analyses) are given under A; the calculated values, according to the formula An^2Ab , under B.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Sp. gr.
55.64	28.19	1.03	9.79	0.19	0.63	5.48, = 100.94	2.604
55.43	28.40	—	10.35	—	—	5.73 = 100	

The felspar is therefore a labradorite contrary to the usual assumption that the triclinic felspar in andesites consists of oligoclase.

Anorthite, $CaAl_2Si_2O_8$. This mineral occurs as a constituent of the eukrite of Hammerfest in Norway (Descloizeaux, *Zeitschr. geol. Ges.* xxvii, 456, 955).

On Anorthite from the Pesmeda Alp, Tyrol, see p. 91 of this volume.

Microcline. This mineral species, first distinguished by Breithaupt (iii. 1014), includes a number of potassium felspars poor in sodium. Its separate identity has been confirmed on optical grounds by Descloizeaux (*Zeitschr. geol. Ges.* xxvii, 456, 955; *Ann. Chim. Phys.* [6], ix. 433), who refers to it a number of amazon-stones, the red felspar of Arendal, several white and green felspars from Greenland, also chertolite; whereas the opalescent felspar of Frederiksvärn (Breithaupt's original microcline), and the green felspar of Bodenmais are orthoclases. Perthite is regarded by Descloizeaux as a mixture of different varieties of orthoclase, not of orthoclase and albite.

The purest microcline is that from Magnet Cove, Arkansas, whereas most microclines—including all the amazon-stones and a number of other felspars hitherto mistaken for orthoclases—are mixtures of microcline with orthoclase and albite, the admixture of the latter often amounting to a fourth of the entire mass. The characterisation of a felspar as microcline can be effected only by optical examination, as the magnitudes of the angles of the crystals are deceptively near those of orthoclase. The colouring principle of amazon-stones is not a copper-compound, as it disappears on heating.

The three following microclines, the sodium of which is regarded by Descloizeaux as entirely due to admixed albite, have been analysed by F. Pisani: (1). From Magnet Cove: purest microcline. (2). Amazon-stone from Muránska, containing only a small amount of enclosed albite. (3). Mineral Hill, Pennsylvania: light green, with broad laminae of albite:

SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	Loss by fusion	Sp. gr.
64.30	19.70	0.74	15.60	0.48	0.35 = 101.17	2.54
65.55	20.30	—	13.90	1.66	— = 101.41	2.576
64.90	20.92	0.28	10.95	3.95	0.20 = 101.20	2.57

These analyses seem to indicate that the specific gravity of a microcline increases with its proportion of soda. Descloizeaux, however, has shown by the examination of numerous microclines, that no such relation exists. This may be seen from the following examples:

1. Green microcline from the Ural.
2. Rose-coloured from Broys, Dép. Saône-et-Loire.
3. Red from Arendal.
- 4 and 5. Amazon-stones from the Ural.
6. Green microcline from the United States.
7. White from Brazil.
8. Rose-coloured from Greenland:

	1	2	3	4	5	6	7	8
Amount of sodium	1.6	2.10	3.25	1.27	1.66	Very rich in Na_2O		
Specific gravity	2.54	2.548	2.543	2.56	2.562	2.56	2.569	2.57

FERMENTATION. The theory of fermentation and the nature and origin of ferments have lately been made the subject of numerous researches, but the results obtained by different experimenters are in many cases very discordant. According to Brefeld (*Dent. Chem. Ges. Ber.* vii. 281), yeast requires for its growth and propagation the presence of free oxygen, and excites fermentation when it is excluded therefrom, but placed under conditions otherwise favourable to its growth. Consequently the free oxygen contained in liquids in which yeast grows is soon absorbed, and then fermentation sets in. The two phenomena of growth and propagation without fermentation, and fermentation without growth and propagation, can be easily separated. If all oxygen is excluded, yeast, before it dies, decomposes an enormous amount of sugar, and produces pure carbon dioxide. In brewers' wort the two reactions proceed simultaneously—fermentation where no free oxygen exists in the liquid, and growth of yeast where oxygen is present. A. Mayer (*ibid.* 579) agrees in the main with Brefeld's conclusions, but thinks that no satisfactory proof has been given of the absolute inability of breathing and growing yeast-cells to induce fermentation. M. Traube (*ibid.* 872) also finds that fresh yeast is not produced in the absence of free oxygen,

even in fermentable liquids which rapidly develop yeast when exposed to the air. Ready-formed yeast can, however, grow in the absence of free oxygen, but in this case the oxygen required for its growth appears to be derived, not from sugar, but from albuminoid substances, since unaltered sugar was found in the liquid after the yeast had ceased to grow. When oxygen is excluded, yeast can induce fermentation in pure sugar-solutions, but in this case the yeast does not increase. In connection with these results, Traube has further observed (*ibid.* vii. 115) that *platinum black*, which has a great tendency to promote oxidation, acts upon sugar in aqueous solution at 150°–160° in the same manner as yeast, with evolution of carbon dioxide and formation of a volatile product smelling like acetic ether. Experiments leading to conclusions opposed to those of Brefeld have been made by J. Moritz (*ibid.* 156, 434; *Chem. Soc. Jour.* 1874, 599); see also F. Mohr (*Ber.* vii. 1421). According to Pasteur, also (*Compt. rend.* lxxx. 452), the yeast-germs produced by alcoholic fermentation can develop themselves in the absence of free oxygen, the fermentation under these conditions going on to its complete termination. He thinks that Brefeld cannot have worked with young yeast, and that the yeast with which Traube experimented must have been impure.

On the theory of Alcoholic Fermentation, see also H. Karsten (*Arch. Pharm.* [3], vii. 55; *Jahresb. f. Chem.* 1875, 892).

Wartha (*Deut. Chem. Ges. Ber.* vii. 1421) finds that in alcoholic fermentation the quantity of alcohol increases during the first hours, while that of sugar diminishes, the temperature quickly rising to 33°, and the cells of the ferment rapidly increasing, but afterwards diminishing and gradually disappearing. During this time, the quantity of alcohol remains stationary, but at the same time considerable quantities of sugar are used up for the formation of yeast-cells.

Pasteur (*Compt. rend.* lxxviii. 213) has prepared a fermentable liquid by dissolving the purest sugar-candy in water with addition of a little yeast-ash, an ammonium salt and a scarcely weighable quantity of pure yeast. In this liquid a considerable quantity of yeast was formed, which must have derived its nitrogen, phosphorus, and sulphur from the mineral substances present, while the sugar disappeared completely without undergoing any fermentation other than alcohol. This result shows that the nutrition and vital processes of the yeast are intimately related to the progress of the alcoholic fermentation. According to A. Trécul (*Compt. rend.* lxxviii. 217), this experiment does not disprove either the spontaneous formation of yeast, or its conversion into *Penicillium*.

Alcoholic Fermentation by Mucor racemosus.—This fungus grows in a solution of milk-sugar without producing fermentation or inverting the sugar; but if the sugar be inverted by an acid, the fungus acts as ferment. *Mucor racemosus* also does not produce fermentation in a solution of inulin, but readily in levulose prepared from it.

When *Mucor racemosus* is added to must containing various proportions of glucose, fermentation easily sets in at 25°–30°, but ceases as soon as 2.5 per cent. of alcohol is formed, whereas the action of *Mucor Mucor* ceases when the liquid contains 0.5 per cent. (A. Fitz, *Deut. Chem. Ges. Ber.* ix. 1352).

Fermentation of Glycerin, Mannite, Starch, and Dextrin, under the influence of Schizomycetes (Fitz, *ibid.* ix. 1348; x. 276; xi. 42).—Redtenbacher found that when a mixture of glycerin, water, and yeast ferments, it yields acetic and propionic acids; and Berthelot obtained alcohol by fermenting a solution of glycerin with chalk and casein. Fitz has obtained quite different results by using a mixture of 2000 water, 100 glycerin, 1 potassium phosphate, 0.5 magnesium sulphate, 2 German pepsin, and 20 chalk, to which a trace of a schizomycetes (p. 782) was added. At a temperature of 40° the liquid soon begins to ferment, carbon dioxide and hydrogen being given off, and the fermentation is completed in ten days. The solution then contains normal butyl alcohol and normal butyric acid, besides a little ethyl alcohol, and a higher acid, probably caproic. 100 parts of glycerin yielded 7.7 pure butyl alcohol and 12.3 anhydrous calcium butyrate.

Glycerin.—When schizomycetes are sown in a fermentable liquid containing a large proportion (say 10 per cent.) of glycerin, rapid fermentation sets in after a day or two and ceases in about fourteen days, though much of the glycerin still remains undecomposed. The mycelium of the fungus has then entirely disappeared, the sediment containing only inactive spores. If now the liquid be decanted and distilled to remove the butyl alcohol formed in the fermentation, and poured back upon the sediment, the spores vegetate and multiply afresh, and rapid fermentation again sets in. Hence it is expedient to employ solutions containing not more than about 3 per cent. of glycerin. Fermentation being over, the liquid is to be decanted from the sediment, the butyl alcohol distilled off, the residue, after cooling, returned to the sediment, and about 3 per cent. of glycerin added, with enough water to make up the

original volume. The accumulation of calcium butyrate and caproate which thus takes place does not affect the schizomyces.

Ammonium sulphate or phosphate may be substituted for pepsin in the fermentable liquid with good results. A liquid containing 150 parts of glycerin, 1.5 of potassium phosphate, 0.7 of magnesium sulphate, 6 of ammonium sulphate, and 30 of calcium carbonate, in 3000 pts. of water, was rapidly brought into fermentation by an infinitesimal quantity of schizomyces, the alcohol thereby formed being chiefly normal butyl alcohol.

The yield of crude alcohols in the experiments just described was about 14 per cent. of the glycerin employed, a very small portion only boiling at a lower temperature than butyl alcohol. Other products of the fermentation of glycerin were caproic, butyric, and probably lactic acids, and a volatile base not yet examined.

Mannite.—A 5 per cent. solution of mannite containing either pepsin or ammonium sulphate yielded by fermentation with schizomyces, normal butyl alcohol and ethyl alcohol, together with butyric, caproic, acetic, succinic, and lactic acids.

Starch.—A trace of schizomyces introduced into a liquid composed of 100 parts of starch, 0.1 of potassium phosphate, 0.02 of magnesium sulphate, 1.6 of ammonium phosphate, 40 of chalk, and 3,000 of water, set up fermentation in twenty-four hours. The products were a little alcohol, chiefly ethylic, 35 per cent. butyric and 9 per cent. acetic acid, with a small quantity of succinic acid.

Dextrin yielded more alcohol than starch.

Milk-sugar is readily made to ferment by schizomyces (but not by saccharomyces, as formerly believed), yielding, amongst other products, about 3 per cent. alcohol, chiefly ethylic.

Dulcitol yields a little alcohol, much volatile acid (chiefly butyric) and a trace of non-volatile acid.

Quercitol yields normal butyric acid only.

• **Butyric Fermentation.**—Baudrimont (*Compt. rend.* lxxx. 1278) has observed the occurrence of spontaneous butyric fermentation in a solution of crystalline cane-sugar. From the gelatinous mass formed in the liquid after twenty-four hours, alcohol separated a nitrogenous ferment containing 0.5 per cent. ash and 5.5 nitrogen.

In the neutral volatile products of the lactic and butyric fermentation of glucose, and in the sour waters of starch factories, Bouchardat (*Compt. rend.* lxxviii. 1145) found ethyl alcohol, normal propyl alcohol, and butyl alcohol, but no pseudo-propyl alcohol, the oxidation-products not containing acetone.

Butyric Fermentation in Water-plants.—From observations by J. Boshm (*Dent. Chem. Ges. Ber.* viii. 634), it appears that land-plants, and many marsh-plants, when immersed in water free from air, undergo a spontaneous butyric fermentation; true water-plants, under the same circumstances, give off marsh-gas, the evolution of which is often preceded by butyric fermentation; but if the plants be previously boiled with water, no evolution of marsh-gas takes place, and the occurrence of butyric fermentation is retarded. If, however, the same plants, after being boiled, and washed with water in an open vessel, they will afterwards give off marsh-gas when immersed in water. The liquid remaining after the butyric fermentation contains free ammonia, and the plants themselves undergo partial and gradual carbonisation (conversion into peat). In accordance with these facts, Boshm ascribes the evolution of marsh-gas from decayed vegetables to a process of fermentation, and represents the decomposition of the cellulose by the equation :



Butyric Fermentation induced by *Elodea canadensis*.—The fermentation of a sugar-juice in which twigs of *Elodea canadensis* were immersed, yielded butyric acid and ethyl butyrate, with evolution of carbon dioxide and hydrogen. The fermented juice also contained alcohol-yeast (Schützenberger, *Compt. rend.* lxxx. 328, 497).

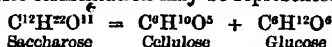
• **Cellulosic Fermentation.**—This name is applied by E. Durin (*Compt. rend.* lxxviii. 128) to a peculiar fermentation which he observed in beet-juice, resulting in the formation of a white hard substance; the same effect was also produced in a solution of beet-molasses by the action of the organisms deposited from the juice of beet. The white substance thus formed exhibited the characters of cellulose, being insoluble in boiling dilute potash, soluble in an ammoniacal solution of cupric oxide (Schweizer's reagent, i. 820) converted by dilute sulphuric acid into dextrin and sugar, and by nitric acid into oxalic acid.

The mother-liquor separated from the cellulose deposited, on addition of alcohol, a white amorphous caoutchouc-like substance, agreeing with cellulose in composition, but swelling up in water, and differing from cellulose in its other physical properties. One or the other of these bodies is formed in greatest abundance, according to the

circumstances of the reaction. They are formed only from saccharose, not from glucose or mannite or any other kind of sugar, and their formation has nothing to do with mucous or viscous fermentation.

On adding some of the cellulose lump to a solution of pure cane-sugar, a new and abundant crop of them was obtained, and the remaining solution was found to contain not only traces of saccharose and of the gummy cellulose, but considerable quantities of levulose.

The process of cellulosic fermentation may be represented by the equation



No gas is evolved when the action goes on in this way; but if the liquid is acid, carbon dioxide is given off, and a considerable quantity of acetic acid is formed. Calcium carbonate favours the transformation, first by keeping the liquid neutral, and secondly, by a special reaction. Barium carbonate, magnesium carbonate, calcium chloride, ammonium salts and nitrates, retard it; the two latter also induce the formation of mould.

The ferment which induces the cellulosic fermentation is nearly related to diastase. A recently prepared solution of diastase acted indeed on a solution of sugar in the same manner as the cellulose clots, excepting that it led to the production, not of these clots, but of the body precipitable by alcohol. A similar but weaker action is exerted by the albuminoids of urine.*

The formation of cellulose from saccharose likewise takes place under the influence of certain fatty seeds, like those of rape or colza. Durin considers that the formation of cellulose in living plants is effected in like manner by the action of ferments on saccharose, and experiments made on sugar-canes, maize-plants, and St. John's bread (fruit of *Ceratonia siligua*), have established beyond doubt that the formation of wood is attended with a decrease in the amount of cane-sugar, and an increase in that of fruit-sugar (*Compt. rend.* lxxxii. 1078).

Viscous or Mucous Fermentation.—Baudrimont (*ibid.* lxxx. 1253) observed the occurrence of a spontaneous viscous fermentation in a solution of crystallised cane-sugar. From the gummy mass produced after twenty-four hours, alcohol separated a ferment containing 0.5 per cent. ash and 5.5 nitrogen.

On Viscous Fermentation, see also Commaille (*Monit. scient.* [3], 435, 673, 772).

Fermentation of Fruits.—From experiments by Lechartier a. Bellamy (*Compt. rend.* lxxix. 949, 1006), on the fermentation of cherries, gooseberries, figs, lemons, cherry and gooseberry leaves, chestnuts, and barley, also of turnips and potatoes, it appears that the life in the cells does not cease with the separation of the fruit, seed, or leaf from the plants, but continues, if the air be excluded, with decomposition of sugar and production of alcohol and carbon dioxide. As soon as the evolution of carbon dioxide ceases, the life within the cell becomes completely extinct. Fruits, seeds, and leaves may continue in this sluggish condition for an indefinite time, provided that no ferment is developed within them.

Lechartier & Bellamy have also examined the action of antiseptic and toxic vapours on the fermentation of fruits. Green apples weighing about 49 grams were placed in flasks containing severally phenol, camphor, and a piece of potassium cyanide. As a means of comparison, one flask was also taken, containing the apple with atmospheric air only. This latter apple gave off, in forty-nine days, 404 c.c. of gas, and from that time till the end of the experiment, viz., seven months, it remained completely inert. Under the influence of phenol and hydrocyanic acid, no gas was evolved in the course of eighty-three days, but in the case of the apple surrounded by camphor-vapour, 16 c.c. were given off. It would, therefore, appear that the action of camphor-vapour is less energetic, and diminishes, without completely destroying, the vitality of the cells (*Comptes rendus*, lxxxiv. 1035).

Similar results have been obtained by U. Gayon (*ibid.* 1036), who also finds that ether and chloroform act in the same way as phenol, while carbon sulphide seems to act in the same way as camphor.

Pasteur (*Compt. rend.* lxxxiii. 173) observes that the stalks of grapes, cherries, strawberries, and gooseberries, are covered with yeast-germs to a much greater extent than the berries themselves, which are sometimes quite free from them. Unripe fruits, and fruits grown in glass houses, are quite free from yeast-germs; so likewise are grapes preserved by the action of water-vapour. After a certain time

* With reference to these statements, Pasteur (*Compt. rend.* lxxxiii. 176) observes that in 1861 he discovered two ferments which induce viscous fermentation; one of which, consisting of chains of small granules, induced the formation of mannite and carbon dioxide together with a viscous body; while the other, which was made up of irregular cells of the size of those of beer-yeast, formed only the viscous mass. The latter would probably excite the cellulosic fermentation described by Durin.

the germs die. The air of Paris was found to contain the same germs, but for the most part only in summer. The observed species were *Saccharomyces past.*, *S. ellips.*, *S. apie*, and *Mycoderma vini* or *cerevisie*.

L. Frémy (*ibid.* 180) observes that well-washed cherries in good condition, kept in an atmosphere of hydrogen or carbon dioxide, remain hard, and for the most part do not crack, but appear opaque internally, and contain yeast-cells even close to the kernel. At the same time, carbon dioxide and alcohol are abundantly formed and the cherries lose their sweet taste. Frémy regards these effects as confirmatory of his theory of intracellular fermentation. Pasteur, on the contrary (*ibid.* 182), finds that these appearances take place in fruits only when they are injured, and consequently the yeast-germs on the surface are carried into the inside of the fruit. The same view is taken by Dumas (*ibid.* 852), and confirmed by the experiments of Joubert and Chamberland (*ibid.* 354) on cherries, gooseberries, and plums kept in carbon dioxide over mercury. These observers suggest that during the washing of the fruits and their introduction into flasks in Frémy's experiments, the skins may have been injured, and a way thereby opened for the penetration of the yeast-germs.

Nature and Origin of Ferments. Ferments are of two kinds: chemical or unorganised, such as diastase, emulsin, myrosin, the ferment of the pancreas, &c.; and physiological or organised, such as yeast, mycoderma, microsomes, bacteria, &c. A mode of distinguishing between the two is afforded by the action of *chloroform*, which kills the latter, but does not produce any alteration in the former. Thus chloroform arrests the fermentation of sugar, but does not interfere with the action of emulsin on amygdalin (A. Müntz, *Ann. Chim. Phys.* [5], v. 428).

Unorganised ferments may be extracted from the vegetable and animal organs in which they occur by means of *glycerin*: in this manner diastase may be extracted from germinating wheat and barley, emulsin from sweet almonds, and animal sugar-forming ferment from the glands which produce it. The fresh glands are comminuted as quickly as possible, freed from blood by washing with water, then dried in the air, finely pulverised, and the powder, after being sifted through fine gauze, is well triturated with glycerin. The ferment may be precipitated from the glycerin-solution by alcohol, and obtained, by repeated solution and precipitation, in the form of a powder almost entirely free from albuminoids, and very effective in converting starch into sugar (v. Wittich, *J. pr. Chem.* [2], ii. 139).

The ferment of the pancreas may also be prepared by extraction with glycerin and precipitation with alcohol. It is a snow-white powder, exhibiting no trace of organisation, in fact, perfectly amorphous; it contains sulphur and nitrogen, and leaves, when burnt, a residue containing sodium and magnesium phosphates. It rapidly converts boiled starch into sugar at ordinary temperatures. Flocks of fibrin, boiled or raw, are gradually attacked by it at 30°, and in the end are completely digested. On leaving a few granules of it for a night at 40° in contact with water and a few drops of olive-oil, the mixture after agitation showed a decided acid reaction. The pulverulent preparation is not hygroscopic, and does not lose weight even after prolonged heating at 100°; neither does it lose its activity at that temperature. In its chemical behaviour it exhibits the closest resemblance to albumin precipitated by alcohol, differing from it indeed only in its capability of redissolving in distilled water. The coagulation of its solution in water or glycerin by boiling is attended with the loss, both of its power of digesting fibrin, and of its diastatic and fat-decomposing action. This coagulation is the consequence of the resolution of the ferment into two bodies, one of which remains in solution, while the other is precipitated (G. Hüfner, *J. pr. Chem.* [2], v. 372).

The salivary glands, the lungs, and putrefying cheese, when treated as above with glycerin and alcohol, yield substances which digest fibrin as readily as the pancreas-ferment, and likewise act like diastase. A comparison of the analyses of the ferments obtained from the pancreas, salivary glands and lungs, and from cheese, also of that of emulsin, according to Buckland Bull (ii. 486), with the analyses of egg-albumin, leads to the inference that all ferments isolated according to the more exact methods now in use, differ essentially in composition from the albuminoids; and their higher content of oxygen renders it probable that they are produced chiefly by oxidation of (Hüfner, *loc. cit.*)

The energy with which the pancreas ferment acts on fibrin does not depend on the presence of oxygen either gaseous or absorbed, and the evolution of combustible gases with which it is more or less attended, is not to be attributed solely to deficiency of oxygen. When the fibrin-decomposing ferment of the pancreas acts alone, and in the absence of all organisms capable of exciting putrefaction, no combustible gases are evolved, but only carbon dioxide; and the development of this last gas is entirely independent of the activity of the ferment, being the result of a process of oxidation

which goes on in its absence. The occurrence of combustible gases is probably due to the action of microscopic organisms (bacteria) (Hüfner, *J. pr. Chem.* [2], x. 1; xi. 43).

J. Munk (*Chem. Centr.* 1876, 622) regards the ferments obtained from saliva, and from the pancreas, as different from that of the muscles, stomach, and intestines, inasmuch as the action of the former is strongly developed in acid and alkaline liquids within certain degrees of acidity and alkalinity, whereas that of the latter is apparent only in neutral liquids.

The following observations on liver-ferment, and on the action of albuminous substances on glycogen, have been made by Seegen a. Kratschmer (*Pflüger's Archiv. f. Physiologie*, xiv. 593):

(1.) The albuminous tissues of the animal body as well as other albuminous substances which are soluble either partly or entirely in water, when left in contact, for a longer or shorter time with glycogen, exert a saccharifying action. By boiling the aqueous solution of the albuminous bodies, the diastatic action is momentarily arrested, but appears again after the space of two or three days. The minutest quantities of soluble albumin are sufficient to exert this sugar-forming action.

(2.) The action of these albuminous bodies on glycogen is qualitatively identical with that of saliva and of pancreas-extract. There is, however, considerable difference both in the quantity and also in the rapidity of the action. The time required is longer, and the sugar formed by the action of albuminous bodies is much smaller in quantity than in the case of saliva or the pancreatic extract. The formation of sugar in a boiled liver is to be referred to the diastatic action of the albuminous tissue contained therein; whereas, in fresh *unboiled* liver, it is highly probable that, as in saliva and the pancreatic juice, a diastatic ferment is present in large quantity.

(3.) No method is known at present by which liver-ferment can be isolated. By all methods hitherto employed, glycogen is first extracted, and this contains, mixed with it, a diastatic element.

(4.) In a pure solution of glycogen in glycerin, ferments are inactive. The formation of sugar occurs immediately when water is added to the mixture.

Ferment of Urine.—Musculus (*Deut. Chem. Ges. Ber.* ix. 1352) has found in the urine of persons affected with catarrh of the bladder, a ferment which is precipitated by alcohol as a conglum resembling fibrin. After drying at a comparatively low temperature, it dissolves in water and is precipitated from the solution by alcohol and acetic acid, but not by sodium chloride. With mercury nitrate it forms a precipitate which becomes reddish on boiling. The aqueous solution mixed with urea and heated to 35°–40° decomposes the urea completely, with formation of ammonium carbonate. The ferment, however, does not possess this decomposing power if it has been precipitated by acetic acid, or heated to 80°; and the same effect is produced by hydrochloric acid diluted to one-thousandth, also by sulphuric, tartaric, acetic, salicylic and other acids, but not by phenol. Dilute alkalis and sodium chloride have no effect. Hydrochloric acid of one-thousandth likewise destroys the fermentative action of diastase; whereas, that of the pancreatic juice and of the saliva is not affected by hydrochloric acid of any degree of concentration below 1 in 100. Acetamide and oxamide treated with this ferment give off only traces of ammonia; hippuric and uric acids, creatine and guanidine are completely decomposed by it, but only after several days.

Bee-ferment.—The head, thorax, and abdomen of working bees contain ferments soluble in glycerin, which completely invert cane-sugar and convert starch into dextrin and sugar. The so-called bee-bread, and the pollen of firs and pines, also contain a ferment which inverts cane-sugar.

Plant-ferments.—The clear aqueous and glycerin extracts of malt, beet, carrots, and yeast, yield, when treated with ether, protoplasmic formations of hyaline structure, some of which (from malt and yeast) act as ferments. These bodies exist in the extracts, not in solution, but in a tumefied gummy condition, and the ether when shaken up with the liquid, mechanically carries the protoplasmic bodies upwards in the form of a jelly resembling frog-spawn, which may be freed from the greater part of the ether by agitation. On washing the remaining mass with water, and then adding strong alcohol, the pure substance separates in the form of a flocculent precipitate, which may be dried under the air-pump (Zulkowsky a. König, *J. pr. Chem.* [2], xi. 43).

Vetch-seeds contain a ferment which converts starch into sugar and albuminoids into peptones. It may be extracted by glycerin from the seeds previously exhausted with alcohol, precipitated from the glycerin-solution by a mixture of alcohol and ether, and purified by repeated solution in glycerin, and precipitation with alcohol

and ether. The ferment contains nitrogen and sulphur, is soluble in water, as well as in glycerin, and leaves when burned a considerable quantity of ash (v. Gorup-Besanez, *Deutsch. Chem. Ges. Ber.* vii. 143, 569).

Hemp-seed and linseed treated as above likewise yield a diastatic and peptone-forming ferment (H. Will, *ibid.* viii. 1510).

The buds and young leaves of trees yield, according to Kosman (*Compt. rend.* lxxxi. 406), ferments which convert saccharose into glucose, starch into dextrin and glucose, and resolve digitalin into glucose and digitaliretin. This ferment has been obtained from the buds of *Ulmus campestris*, *Populus nigra*, *Quercus pedunculata* and *Corylus avellana*; from the flowers of *Cornus sanguinea* and *Prunus spinosa*; and from the young leaves of *Chelidonium majus* and *Digitalis purpurea*.

Organised Ferments. The question as to the spontaneous generation of organised ferments in organic liquids, has lately given rise to considerable discussion. According to C. H. Bastian (*Proc. Roy. Soc.* xxv. 149), bacteria are formed in normal urine having an acid reaction and free from spores, after it has been heated to 50°; also in the same urine when it is neutralised with potash after being heated; or when, after previous heating to 50° or even 100°, it is subjected, in the neutralised state, to the action of electrolytic oxygen. In all cases the formation of bacteria was very considerable, even after 7 to 12 hours. Tyndall, on the other hand (*ibid.* xxiv. 171), finds that air enclosed in a box, the inner surface of which is carefully coated with glycerin and left for several days, so that all particles of dust, and with them all organic germs, may have settled to the bottom, is incapable under any circumstances of inducing putrefaction, either in vegetable or in animal fluids, such as urine. The same is the case with filtered air, and with air which has been passed through a red-hot tube. He further observes that the alkaline nature of a liquid never promotes the formation of germs. These negative results were obtained when the liquids were enclosed in flasks from which the air had been expelled by boiling. Tyndall further points out the numerous sources of error to which such experiments are liable, and the extreme difficulty of completely preventing the access of organised germs to the liquids. He finds, moreover, that putrefaction takes place in various ways and with different degrees of rapidity even in liquids of exactly similar constitution exposed to ordinary air under exactly similar circumstances, and explains this result by the assumption that the germs are diffused through the air in cloud-like swarms of various densities, the individual germs being sometimes fresh and moist, sometimes either dead or dry, so that they are either inert or act with diminished energy.

Pasteur also (*Compt. rend.* lxxxi. 176) dissents from Bastian's conclusions. He directs attention to the great improbability of the supposition that a body like potash can act as a generator of living organisms, and points out, as previously shown by Pouchet (*ibid.* lxxiii. 131), that organic germs, though killed when heated to 100° in acid liquids, are not destroyed when heated to the same temperature in neutral or alkaline liquids, a temperature of 110° being required to kill them in that case. Bastian, on the other hand (*ibid.* lxxxi. 562), states that a moderately acid urine, which, according to Pasteur, should have been freed from organic germs by heating to 100°, was found to contain them when left to cool and subsequently heated to 50°, and that a number of organic liquids, in which no formation of organisms took place at 25°, were found to contain them after being heated to 50°. Tyndall, on the contrary (*ibid.* 364), says that he has never been able to detect the formation of organisms in urine by heating to 50°. See further, Tyndall (*Proc. Roy. Soc.* xxv. 457, 503, 569); Burdon Sanderson (*ibid.* xxvi. 322, 416); Tyndall (*ibid.* 228, 353, 487).

According to J. Duval (*Compt. rend.* lxxvii. 1027, and lxxix. 1180) the air never contains really-formed ferments, but only their germs, such as the spores of fungi or cells of the lower algae, which in certain media develop into ferments, whose nature is determined by the constitution of the media themselves, so that one ferment may be converted into another by a particular alteration of the medium.

Can Organisms continue to live in the complete absence of Oxygen?—The following experiments bearing on this question have been made by G. Hüfner (*J. pr. Chem.* [2], xiii. 475). A number of flasks containing water and a small quantity of fibrin were emptied of air by prolonged boiling, then sealed, and a quantity of putrefying liquid contained in a side-tube fused into each of the flasks was made to flow into it. All the flasks were found to be quite free from air, and after standing for a fortnight at 30°, the liquid in them still contained numerous living bacteria. The gas evolved in them consisted of hydrogen and carbon dioxide, in one case 42.66 and 57.34 per cent. respectively, in another 22.28 and 77.72 per cent.

Bacteria in Putrefied Blood.—V. Feltz (*Compt. rend.* lxxxiv. 358) found that 1 c.c. of putrefied blood containing bacteria when mixed with 5 c.c. of water and injected into the veins of a rabbit, killed it in three to seven days. After coagulation by

exposure to a temperature of 80°, it was still full of bacteria, and proved fatal to a rabbit in eight days. But when the putrefied serum was exposed to a temperature of 160° in a sealed tube for four hours, the blood became innocuous. There were then no living organisms visible under the microscope.

Bacteria in Plants.—According to Trécul (*ibid.* lxxx. 95), bacteria may be developed in the interior of compact vegetable tissue.

Bacteria in Sulphuretted Waters.—J. B. Schnetzer (*Ann. Chim. Phys.* [5], vii. 281) found living bacteria and other organisms in the deposit from a natural water containing hydrogen sulphide; and Cohn (*Dingl. pol. J.* ccxxii. 399) found them, together with algae, in the peach-blossom-coloured organisms which live on decaying plants in waters containing sulphates.

Formation of Ammonia and Nitrites by Bacteria.—Meusel (*Ann. Ch. Phys.* [5], vii. 287) observed that water containing nitric acid, and originally free from ammonia and nitrites, contained these compounds after being subjected to the action of bacteria. The reduction of the nitric acid by these organisms was prevented by the presence of phenol, salicylic acid, benzoic acid, alum, and concentrated solution of common salt; but took place with remarkable intensity in otherwise pure water containing only nitrates and bacteria, when carbohydrates were likewise present, and scarcely perceptibly on addition of organic acids. Water freshly distilled and mixed with sugar was not found to reduce nitrates when the air was excluded from it. From these observations it appears that bacteria promote oxidation by acting as carriers of oxygen.

Decompositions effected by the Bacteria of the Pancreas.—An extended series of experiments by Jeannerot (*J. pr. Chem.* [2], xv. 353) has led to the following conclusions: 1. The decomposition of gelatin, albumin, and other nitrogenous compounds, and of carbohydrates, by these organisms, may take place without access of air, but it then proceeds much more slowly than when air is present. 2. The more simple chemical compounds produced by the decomposition are the same, whether air is present or absent. Tyrosine was formed from albumin after twenty-nine days' action, in absence of air, and leucine from gelatin after eleven days' action. These substances were not found after the same lapse of time, when the decomposition proceeded in presence of air. 3. The gases produced in the decomposition of gelatin are almost wholly absorbed by caustic potash. 4. The amount of carbon dioxide produced in the decomposition of albumin and gelatin increases from day to day, as the action proceeds. 5. The pancreas bacteria are produced, and continue to exist, in absence of air; but for their complete activity nitrogen compounds must be present.

Microzymes.—This name is applied by Béchamp to extremely minute living organisms, which are capable of developing into bacteria, and, on the other hand, may be formed from the latter. Beer-yeast introduced into starch was found to disappear and give rise to the formation of microzymes; and, according to Béchamp, any animal cell whatever may be transformed into microzymes. As molecular organised primary cells, these organisms may be detected in the liver, in egg-yolk, and in the pancreas. They are capable of exciting fermentation and putrefaction (*Compt. rend.* lxxx. 494, 1027, 1359; lxxxi. 226); see also Gayon (*ibid.* lxxx. 674, 1096). Béchamp and Pastor (*ibid.* lxxvi. 1143) have observed the mutual conversion of microzymes and bacteria to take place in the alimentary canal of a dog.

According to Béchamp (*ibid.* lxxvi. 1414) the gelatinous precipitate called *glairin* or *haregin* (i. 500) deposited from the sulphur-springs of Molitz in the Pyrenees consists of a collection of microzymes enveloped in a transparent substance. Like all microzymes, those of *glairin* are capable of converting sugar into alcohol and acetic acid, and of developing into bacteria.

Schizomycetes or Splitfungi.—These names are applied by Fitz (*Deut. Chem. Ges. Ber.* xi. 46) to certain species of the lower fungi, which multiply by division, the cell lengthening and forming a transverse division in the middle, and the two new cells thus formed multiplying themselves in the same manner. Most of these fungi can live and multiply only in presence of oxygen, and these (called by Pasteur *Aërobies*) burn the carbon-compounds of the nutritive liquid in which they live, to carbonic acid and water. Those, on the other hand, which are capable of exciting fermentation (Pasteur's *Anaërobies*) can live and multiply in complete absence of oxygen, and it is exactly this absence of oxygen which makes them act as ferments. In presence of oxygen they act like those of the first division, and give rise to the combustion of carbon compounds, but when no oxygen is present, they decompose the fermentable substance. To this latter division belong the ferment-organisms which excite fermentation in calcium lactate and tartrate, glycerin, &c.

The ferment-organisms of the glycerin-fermentation belong to a genus called *Vibrio* by Pasteur, *Bacillus* by Cohn. The most convenient source of them is fresh cow-dung; they appear to be most active at a temperature of 37°–40°. Two species are

distinguished, the broader, called *Butyl-bacillus*, being apparently that which in the fermentation of glycerin gives rise to the formation of butyl alcohol, while the narrower species (*Bacillus subtilis*) gives rise to ethyl alcohol (p. 776). The fermentation of starch by means of *Bacillus subtilis* affords an excellent method of obtaining butyric acid. Fitz's paper above cited gives full details of the methods of cultivating these fungi, and of their microscopical aspects.

Yeast. Preparation of Pure Yeast free from Bacteria.—When ordinary beer-yeast is added to a filtered decoction of yeast to which sugar-candy and alcohol have been added, the products of the action thereby set up vary with the proportions of the ingredients, more especially with the proportion of alcohol. A decoction of 40 grams of yeast in 200 c.c. of water, made up to 1 litre with water holding in solution 100 grams of sugar-candy (Pasteur's liquid), undergoes alcoholic fermentation almost completely on addition of a small quantity of yeast. But if the proportion of sugar be reduced to one-half, the formation of yeast-cells goes on with difficulty, whilst bacteria develop rapidly, and in a few days the liquid becomes putrid. The development of bacteria and of all other disease-forments, as well as of *Mycoderma vini*, is, however, considerably retarded by a small quantity of alcohol (2.8 per cent.), and entirely prevented by a larger quantity (5.6 per cent.) The development of yeast is also retarded by alcohol, but still goes on in solutions containing 8.2 per cent. Pure yeast may therefore be developed in appropriate solutions containing from 5.6 to 8.2 per cent. alcohol. With this proportion of alcohol, however, the temperature must not exceed 15°; at about 25°, even 10.6 per cent. is not sufficient to prevent completely the formation of bacteria: but yeast grown at lower temperatures can afterwards increase, without any contamination from bacteria, in nutritive solutions free from alcohol, even at 35°. The propagation of yeast in a solution rich in albumin at about 30°, affords, therefore, the best criterion of its perfect freedom from bacteria—a point not easy to determine by microscopical examination (Traube, *Deut. Chem. Ges. Ber.* ix. 183; 1239).

Composition of Yeast.—Schützenberger (*Compt. rend.* lxxviii. 493; *Bull. Soc. Chim.* [2], xxi. 204) by boiling fresh yeast containing 29–30 per cent. of dry substance with water, obtained an insoluble residue, amounting only to 20–21.5 per cent.; and when the same yeast, after washing with cold water, was suspended in water and left in it for twelve to fifteen hours at 35°–40°, it gave up to boiling water 17 to 18 per cent. of its substance, the insoluble residue, when dried at 100°, amounting to 12.5–13 per cent. During the digestion, a slow and regular evolution of carbon dioxide took place, attributable to alcoholic fermentation of the sugar formed in the process; when this action ceased, the yeast did not exhibit the least sign of putrefactive alteration. The extract contained: 1. A considerable quantity of phosphates. 2. A large quantity of gum (arabin), convertible by nitric acid into mucic acid. 3. Leucine and tyrosine, to the former of which a sulphuretted compound obstinately adhered. 4. Carnine, xanthine, guanine, hypoxanthine, and sarcosine. When these substances have been removed, there remains a sweetish, uncrystallisable syrup still containing nitrogen. The aqueous decoction of fresh yeast contains the same substances as that of the digested yeast.

According to Béchamp (*Compt. rend.* lxxviii. 645), yeast in a pasty state kept for forty-eight hours at 25°–30° becomes completely liquefied, and if it be then thrown upon a filter, more than half its weight will filter through. A similar result takes place at the ordinary temperature, but more slowly. The liquid product contains alcohol and acetic acid, but no appreciable trace of butyric acid; leucine, tyrosine, gummy matter, &c., are also present, as when yeast is allowed to exhaust itself in presence of water. Yeast which has been used for one or two fermentations does not liquefy spontaneously, at least at ordinary temperatures, even when kept in contact with the air for six months. Fresh yeast contains neither tyrosine nor leucine, those being products formed by a special function of the cellule.

According to Belouhoubeck (*Jahresh. f. Chem.* 1875, 898), 'press-yeast' always contains from 3 to 12 per cent. starch, which is added to it before pressing; also, the fungi, *Saccharomyces cerevisiae* and *S. exiguus*, *Mycoderma aceti* and *Oidium lactis*, together with bacteria. Amongst the chemical constituents are: albumin, gluten, the nitrogenous constituent of the protoplasm, cellulose, amyllum, dextrin, ethyl alcohol; lactic, carbonic, phosphoric, sulphuric, and silicic acids; potash, soda, lime, magnesia, manganous oxide, and ferric oxide.

J. W. Gunning (*Deut. Chem. Ges. Ber.* v. 821) finds that yeast may be deprived of its fermenting power by exhaustion with glycerin. The filtrate does not contain any cells recognisable by the microscope, and does not reduce Fehling's solution,* but quickly converts saccharose into glucose. The exhausted yeast-cells are without action, not only upon a solution of cane-sugar, but also on a solution of glucose, and

do not recover their characteristic property till a little of the ferment-solution is added to them. Gunning further observes that Pasteur's liquid containing cane-sugar, ammonium tartrate, and yeast-ash (p. 776), does not of itself possess the power of nourishing yeast-cells, but becomes nutritive to them in presence of albumin or of ferments.

Sugar-inverting constituent of Yeast. Invertin.—Donath (*Deut. Chem. Ges. Ber.* viii. 795) obtains this substance by treating yeast according to Zulkowsky a. König's method (p. 780). The yeast, after being almost completely exhausted with absolute alcohol, and dried at the ordinary temperature to a brittle mass, is finely pulverised, and thoroughly lixiviated with water at ordinary temperature; the opalescent filtrate is shaken up with ether, and the frogspawn-like mass, after washing with water, is dropped into alcohol and left to dry under the air-pump. It is thus obtained in the form of a powder, a very small quantity of which is sufficient to bring about the inversion of cane-sugar at ordinary temperatures in ten to fifteen minutes. Donath is of opinion that it cannot be regarded as an albuminous substance.

Preservation of Yeast.—Jeverson a. Boldt (*Dingl. pol. J.* cccviii. 467) preserve yeast by washing it carefully, pressing out the water, drying the press-cake in a vacuum in presence of hygroscopic substances, and finally in a stream of gas, and hermetically sealing the dried powder in glasses or boxes. Yeast thus treated keeps for many months, and when required for use may be rubbed up with water at 20°–30° to a thin paste which will act like fresh yeast.

Antiferments or Antiseptics. Dumas found that borax prevents the action of yeast-water upon sugar, of synaptase on amygdalin, and of myrosin on myronic acid (*2nd Suppl.* 517). According to Petit, on the other hand (*Compt. rend.* lxxv. 881), it merely retards the action of yeast upon sugar; and, according to S. Darby (*Pharm. J. Trans.* [3], iii. 742), it only slightly retards the formation of volatile mustard-oil in a mixture of black mustard seed and water, or of benzaldehyde in a mixture of bitter almonds and water. According to J. B. Schnetzler, on the other hand (*ibid.* v. 846), borax destroys the activity of bodies which excite fermentation and putrefaction; it also kills infusoria and the protoplasm of the vegetable cell. Schnetzler also reports, on the authority of A. Robottom, that the carcass of a horse which had lain for four months at a temperature of 45° in a Californian soil rich in borax, was found completely preserved and free from odour. A similar fact is mentioned by Bédoin (*Compt. rend.* lxxxii. 1169, 1189) with regard to the flesh of an ox, and the blood of a horse affected with glanders.

Suillot (*Bull. Soc. Chim.* [2], xxv. 346) recommends for the preservation of meat, the use of calcium borate, B_4O_7Ca , which, according to his observations, is resolved, in contact with the meat, into free boric acid, which prevents the formation of mildew, and a more basic salt which prevents the putrefaction. Free boric acid does not act antiseptically; the crystalline compounds of hydrated calcium borate with glucose or saccharose decolorise the meat, but do not prevent the formation of mildew.

According to Laujorais (*Compt. rend.* lxxxiii. 579), potassium dichromate acts as an antiseptic.

According to Petit (*Compt. rend.* lxxv. 881), a solution of 50 grams of cane-sugar in 1 litre of water mixed with yeast in the proportion of 0.5 gm. to 10 c.c. of liquid ferments slowly but regularly when mixed with 1 per cent. ferrous sulphate; with 1 per cent. cupric sulphate the fermentation begins, but soon ceases; 1 per cent. phosphorus, and small quantities of turpentine-oil, mustard-flour, tartaric and sulphuric acids, and cresote produce no retardation; 1 per cent. arsenious acid retards the fermentation, which, however, goes on regularly; $\frac{1}{4}$ per cent. oxalic acid produces considerable retardation; $\frac{1}{4}$ per cent. acetic acid appears to retard the fermentation to a greater degree than the mineral acids. Sulphites do not retard fermentation, but are themselves converted into sulphates during its progress. Mercuric oxide appears to be the most powerful of all antiseptics, and next to it mercuric chloride; 0.5 per cent. of mercuric oxide is sufficient to put an immediate stop to fermentation in active progress. According to Bucholtz, an aqueous solution of mercuric chloride, containing 1 pt. of the salt in 20,000 of water, exerts an antiseptic action equal to that of aqueous salicylic acid containing 1 pt. in 666, or of aqueous alcohol containing 1 pt. in 50.

Formic acid, even in extremely small quantity, prevents fermentation, but its salts do not (Ziegler, *Jahresb. f. Chem.* 1874, 953).

S. Bidwell (*Pharm. J. Trans.* [3], vi. 746) has compared the preservative properties of phenol, chloral hydrate, salicylic acid, and benzoic acid on meat kept under water, and finds that, for equal quantities, benzoic acid is the most efficacious; further, that salicylic acid acts better when mixed with hydrochloric acid than when alone.

On the Antiseptic Action of Salicylic Acid, see further BENZOIC ACIDS (oxy-) (p. 286).

Thymol has been used with good effect as an antiseptic, by Paquet (*Bull. général de la thérapeutique*, 1868) in the hospitals of Paris, instead of the insufferably smelling carbolic acid. Its antiseptic power has been compared with that of carbolic acid (phenol) by Peschechonow (*Russ. Zeitschr. Pharm.* xii. 609), who finds that thymol retards the action of saliva on starch, and much more powerfully that of pepsin on albumin. Its influence on both these digestive fluids increases with the quantity added, and is slightly superior to that of phenol.

On the Purification of Putrid Waters by the Roots of Living Plants, see Jeannel (*Ann. Chim. Phys.* [5], v. 571).

On the Preservation of Fruit, and the Action of Antiseptic and Toxic Vapours on Fruit Fermentation, see p. 778.

FERN. The roots of the male fern (*Lastrea Filix mas*, *Aspidium Filix mas*), gathered near Wolmar, in April, July, and October 1874, have been analysed by Kruse (*Arch. Pharm.* [3], ix. 24), with the following results:

	Dried at 100°.	April	July	October
Moisture in the air-dried root		15.7	13.4	13.5 per cent.
Ash of roots dried at 100°		2.2	2.5	2.5 "
Aqueous extract (dry)		36.4	25.4	35.8 "
Alcoholic extract, after extraction with water		27.3	26.1	39.5 "
Ethereal extract		10.3	12.4	11.5 "
Petroleum spirit extract		9.3	8.4	9.1 "
Amylum		28.2	22.7	15.4 "
Tannic acid, by precipitation with copper acetate		4.6	6.9	5.9 "
Tannic acid, by precipitation with lead acetate		9.2	9.8	11.7 "
Filix-red		5.2	6.9	7.8 "
Gum and albumin		5.5	2.3	2.1 "

FERRO- and FERRI-CYANIDES. See CYANIDES (pp. 611-616).

FERULIC ACID, $C^{10}H^{10}O^4 = C^6H^5 \begin{matrix} \diagup CH=CH-COOH \\ \diagdown OCH^3 \\ \diagdown OH \end{matrix}$ (Tiemann u. Nagai,

Deut. Chem. Ges. Ber. ix. 52). This acid may be prepared synthetically by digesting

sodium-vanillin, $C^8H^8O^3 \begin{matrix} \diagup COH \\ \diagdown OCH^3 \\ \diagdown ONa \end{matrix}$, with excess of acetic anhydride and fused sodium

acetate for four or five hours in an oil-bath at 150°-160°, with reflux condenser, treating the product with water, and dissolving the viscous residuum in ether. The ethereal solution, freed from simultaneously formed aceto-vanillin by agitation with acid sodium sulphite, leaves on evaporation, vanillin-coumarin,

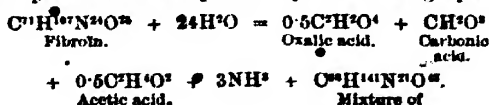
$C^{10}H^8O^4 = C^6H^5(OCH^3) \begin{matrix} \diagup CH=CH \\ \diagdown O-CO \end{matrix}$, which may be purified by washing with alcohol

and frequent crystallisation from glacial acetic acid. This compound, boiled with alcoholic potash, is converted by addition of H^2O into ferulic acid, which may be isolated by the usual methods.

Ferulic acid thus obtained dissolves easily in alcohol and ether, sparingly in cold, easily in hot water, and may be purified by crystallisation from the latter. It is identical with ferulic acid prepared from asafetida, and both the natural and the synthetically formed acid melt at 168°-169°, not at 153°-154°, as commonly stated.

FIBRIN. See PROTEINS.

FIBROIN. Cramer assigned to this substance the formula $C^{13}H^{12}N^4O^8$ (1st *Suppl.* 1024). Schützenberger u. Bourgeois (*Compt. rend.* lxxxi. [191], from a study of the products obtained by boiling it with baryta-water, have deduced a more complex formula, and represent the decomposition by the following equation:



E. Durrwell (*Bull. Soc. Chim.* [2], xix. 447), by treating fibroin with sulphuric acid, has obtained a compound of the two bodies, the composition of which has not however been determined.

3rd *Sup.*

FIBROLITE. This mineral occurs as a pseudomorph after corundum at Mineral Hill, Delaware County, Pennsylvania. The following analyses are by Genth (*Sill. Am. J.* [2], ix. 77). 1 and 2 nearly pure; 3 quite pure:

	SiO ²	Al ² O ³	Fe ² O ³	MnO	MgO	CaO	Loss by ignition.	Sp. gr.
(1.)	87.76	60.27	0.98	—	0.18	0.44	0.73 = 100.36	3.286
(2.)	37.62	60.91	0.94	—	0.24	0.49	0.62 = 100.73	—
(3.)	37.37	60.52*	0.90	0.10	0.25	0.38	0.48 = 100	—

* Determined by difference.

See FERN (p. 785).

On the Action of Glass on Fire-clays at high temperatures, see

CLAY (p. 521).

On the Analysis of Fire-clays, see S. Kern (*Chemical News*, xxxv. 203; *Chem. Soc. J.* 1877, ii. 356).

FISETIN. This name was given by Chevreul to the yellow colouring matter of Fiset-wood (the heart-wood, separated from bark and alburnum, of a species of sumach (*Rhus cotinus*)). This yellow dye-stuff, which crystallises in needles, was regarded by Bolley (*Bull. Soc. Chim.* [2], ii. 479) as identical with quercetin, C²²H¹⁸O²². According to Koch, however (*Deut. Chem. Ges. Ber.* v. 285), fisetin, when carefully purified from a red colouring matter which likewise exists in the wood, gives by analysis numbers agreeing nearly with the formula C¹⁵H¹⁰O⁸, which is confirmed by the composition of its acetyl-derivative, C²⁵H¹²(C²H³O)³O⁴. According to this result, fisetin differs from quercetic acid, C¹⁵H¹⁰O⁷ (v. 8) by containing 1 atom of oxygen less. When fused with an alkali it yields a small quantity of white needles, which give the characteristic reactions of quercetic acid.

FISHES.—Several liquids occurring in the bodies of fishes and crustaceans, have been examined by Rabuteau a. Papillon (*Compt. rend.* lxxvii. 135). The peritoneal fluid of rays, torpedoes, and sharks was found to contain a very small quantity of a peculiar albuminous body, together with considerable quantities of methylamine and urea. The strongly acid gastric juice of the ray yields hydrochloric acid when distilled, and contains bromine in the form of a metallic bromide.

On the Blood of the Sea-spider, of Crabs, and of the Ray, see p. 336.

On the Respiration of Fishes, see RESPIRATION.

FLAME. *Luminosity of Flame.*—Frankland's experiments on the luminosity of flames burning under high pressures (1st *Suppl.* 485) have been repeated and extended by L. Cailletet (*Compt. rend.* lxxx. 487; *Ann. Chim. Phys.* [5], vi. 429), who observed that the flames of candles, sulphur, potassium, and carbon bisulphide, but not of phosphorus, burned in gradually compressed air with continually increasing intensity of illumination up to pressures of 30 to 35 at. The chemical intensity of the light also appeared to increase with the pressure, judging from its increased activity on phosphorescent substances. According to V. Wartha (*J. pr. Chem.* [2], xiv. 84; *Chem. Soc. J.* 1876, ii. 376), stearin candles burning in air under a pressure of 1.96 at., lose from 13 to 17.4 per cent. less than when burning under ordinary pressure. At the higher pressure candles burn with a dull yellowish-red smoky flame, fully twice as long as that of the same candles burning in the open air. Candles burning at a constant pressure of 90 mm. give a large clear non-luminous flame, consisting of an inner bluish-green cone surrounded by a violet stratum, the whole being enclosed by a very faint violet mantle. It is worthy of note, that observations on the burning of candles under reduced atmospheric pressures were made by Boyle; in his account of his early experiments on the vacuum, he minutely describes the appearance of the flame as seen under diminished pressure in the receiver of his 'new pneumatical engine.' The non-luminosity of the flame under low pressures, was supposed by Frankland to be due to the increased mobility of the oxygen molecules in the rarefied air, in consequence of which they were able to penetrate more freely into the interior of the flame. According to Wartha, the differences in the illuminating power of the flames of candles and of other combustibles under varying pressures, are to be attributed to the effect of the pressure on the dissociation-point of the burning substances. Dissociation occurs at a lower temperature under a high than under a low pressure. Hence, when candles are burned in air under very high pressure, the dissociation of the hydrocarbons takes place more rapidly than the products can be burned, and the flame becomes smoky; under reduced pressure the reverse is the case.

It is well known that even a comparatively small admixture of air greatly impairs the illuminating power of coal-gas. Sillimann and H. Wurtz (*Sill. Am. J.* [2], xlviii. 40; *Jahresb.* 1869, 1134) have made a series of observations on this point with the gas of the Manhattan Co. (New York) with the following results:

Sp. gr. of coal gas	0.401	0.392	0.401	0.387	0.387	0.387	0.387	0.403	0.401
Sp. gr. after admixture of air	0.409	0.405	0.421	0.419	0.433	0.467	0.490	0.525	0.5516
Air in 100 pts. of coal-gas	1.06	3.15	1.50	1.61	1.61	1.61	1.61	1.12	1.61
Air in 100 pts. after addition of air	3.01	4.97	3.75	4.61	6.54	13.32	17.79	21.88	26.29
Volume of added air	1.05	1.82	2.25	3.00	4.96	11.71	16.18	20.76	24.68
Illuminating power of coal-gas	15.12	14.67	14.71	14.81	14.81	14.81	14.81	15.09	14.11
Illuminating power after addition of air	14.20	13.27	12.06	12.49	11.28	8.67	6.20	4.09	2.18
Loss in illuminating power.	0.92	1.40	1.75	2.32	3.53	6.14	8.52	11.00	11.93
Percentage loss	6.08	9.54	11.82	15.69	23.83	41.46	57.53	72.90	84.55
Ratio of loss to the per cent. volume of air and gas	5.79	5.24	5.25	5.23	4.83	3.54	3.55	3.50	3.42
Loss in illuminating power for 1 per cent. added air	0.723	0.511	0.582	0.656	0.501	0.419	0.378	0.377	0.380

The burner employed was an argand. Audouin and Bérard have made similar observations with a batswing burner; in this case the effect of the addition of air was more marked.

It has been shown that a coal-gas flame burning in air becomes non-luminous by previous admixture with nitrogen, hydrochloric acid, and carbon dioxide (Knapp); carbon monoxide, hydrogen (Blochmann); or even steam (Sandow). These observations clearly indicate that the decrease in luminosity cannot be ascribed solely to the more energetic oxidation of the carbon contained in the flame.

Wibel has also shown (*Deut. Chem. Ges. Ber.* viii. 226) that when any such mixture is strongly heated before it undergoes combustion, it again becomes luminous; hence he supposes that the absorption of heat arising from the admixture of the chemically indifferent gas, is the main cause of decrease in luminosity.

These observations have been critically examined, and their bearing on the theory of the luminosity of hydrocarbon flames discussed by Heumann (*Liebig's Annalen*, clxxxi. 129; clxxii. 1; clxxiii. 102; clxxiv. 208). Heumann has proved that, the luminosity in Wibel's experiment is actually due to the added heat, and not to any remote cause, such as an alteration in the relative proportion of coal gas and indifferent gas, or in the chemical nature of the gas on heating. Still it does not follow that the non-luminous Bunsen flame has a lower temperature than that of an ordinary gas-flame. The admixture of an inflammable gas having a pyrometric effect scarcely less than that of the coal gas, as, for example, carbon monoxide, causes the flame of the coal-gas to become non-luminous. Hence it would seem that the mere dilution of the burning gas plays an important part, and may of itself, independently of any absorption of heat, cause a diminished luminosity. Heumann concludes that there are at least three causes capable of decreasing the luminosity of flames; viz. withdrawal of heat, dilution, and oxidation of the luminous material. In most cases, two at least of these causes are concerned; in the flame of the Bunsen lamp all three are at work.

If the flame of a candle, or of coal-gas be closely examined, it will be seen that the one does not touch the rim of the burner, nor the other the wick (Blochmann, *Liebig's Annalen*, clxviii. 345). The intermediate space in the case of coal-gas may be increased by mixing it with an indifferent gas, as nitrogen or carbon dioxide. These phenomena are due to the cooling effect of the wick or the burner. Whenever a cold object touches a flame, a dividing space, similar to that noticed between flame and burner, is observed, in size dependent on the coldness of the object, or its specific heat, and the dilution of the burning gas. A thick metallic wire brought into a flame diluted with carbon dioxide, causes a clear space around itself, which increases with the proportion of the indifferent gas. The diluting gas lowers the flame tem-

perature, by diffusing the heat needed to maintain a given quantity of the coal-gas in a state of combustion throughout a greatly increased volume of gas. If the temperature of the flame is already low, the further decrease resulting from the introduction of the cold object suffices to cool a comparatively large extent of gas below the ignition-point, and hence to extinguish the flame in the cooled space.

If the gas issues under great pressure, the space between the flame and burner is considerably enlarged, often to a distance of several decimeters. According to Benevides (*Ann. Chim. Phys.* [4], viii. 358), this cold dark space is due to the mechanical action of the issuing gas in consequence of which the air is driven aside from the orifice of the burner, and prevented from mixing with the gas in sufficient quantity to render the mixture combustible. A flame brought near to the dark space is carried along by the gas stream. On bringing a wire into the flame and moving it into the dark space, the flame follows the wire towards the burner, but on withdrawing the wire, the flame returns to its original position. The production of this dark space is, however, to be traced rather to the cooling action of the gas and air-stream, and to the circumstance that the velocity of the gas stream in the neighbourhood of the burner is greater than the rate of propagation of ignition within the gaseous mixture.

Heumann has also investigated the effect of the material of the burner on the illuminating power of a coal-gas flame, and finds, contrary to the conclusion of the Board of Trade Commission, that a notable diminution of light intensity is caused by the employment of metallic burners as compared with those of steatite; he has also shown that by considerably raising the temperature of the issuing gas and of the burner, a marked increase in luminosity is effected, due to the earlier separation of carbon particles in the flame, and not to any change in the chemical composition of the gas itself. Burners have been constructed in which the temperature of the gas is raised before combustion, but they are of little practical benefit if the heat is derived from the luminiferous flame itself.

Hitherto very little distinction has been drawn between the *light effect* of the whole flame, and the *intensity of light*, i.e. the quantity of light emitted by the various constituent parts of the flame. On the assumption that the light emitted by the luminous constituents is the same in the different parts of the flame, the light effect is equal to the product of the intensity of light into the volume of the flame. Heumann suggests that measures of the light-intensity might be obtained by allowing the rays to pass through a small accurately measured opening in a shade, placed between the flame and the diaphragm of the photometer.

There can be little doubt that the luminosity of a hydrocarbon flame is due, as Davy supposed, to the presence of incandescent solid carbon. Stein has pointed out in reference to Frankland's hypothesis that the illuminating power is due to dense hydrocarbons within the flame, that if the soot be present as vapour in luminous flames, a high temperature after condensation should again cause it to assume the gaseous condition, but soot is absolutely non-volatile even at the highest temperatures. Moreover, the amount of hydrogen which it contains does not exceed 0.9 per cent. Heumann has advanced the following proofs of the presence of solid carbon in luminous hydrocarbon flames.

(1.) *Chlorine causes an increase in the luminosity of feebly-luminous or non-luminous hydrocarbon flames.* Since chlorine decomposes hydrocarbons at a red heat, with separation of carbon, it follows that the increase in luminosity is due to the production of solid carbon particles.

(2.) *A rod held in the luminous flame soot becomes covered on its lower surface, i.e. the surface opposed to the issuing gas, with a deposit of soot.* The solid soot is driven against the rod. If the soot existed as vapour within the luminous flame, its deposition would be due to a diminution of the temperature of the flame, and would therefore occur on all sides of the rod.

(3.) *A strongly heated surface also becomes covered with a deposit of soot.* This result could not occur if the deposit were due to the cooling action of the surface.

(4.) *The carbon particles in the luminous flame are rendered visible when the flame comes in contact with another flame, or with a heated surface.* The separated particles are agglomerated into larger masses, and the luminous mantle becomes filled with a number of flowing points, giving a very coarse-grained soot.

(5.) *The transparency of a luminous flame is no greater than that of the approximately equally thick stratum of soot, which rises from the flame of burning turpentine, and which is universally allowed to contain solid particles.* The luminous flame of hydrogen, containing solid chromic oxide, is as transparent as the hydrocarbon flame.

(6.) *Flames which undoubtedly owe their luminosity to finely divided solid matter, produce characteristic shadows in sunlight.* The only luminous flames incapable of

producing shadows are those consisting of glowing vapours and gases. *Luminous hydrocarbon flames produce strongly marked shadows in sunlight: these flames, therefore, contain finely divided solid matter. This solid matter must be carbon, since no other substance capable of remaining solid at the temperature of these flames is present.*

Bunsen-lamp flame.—The nature of the chemical changes occurring in the non-luminous flame of the Bunsen lamp, has been studied by Blochmann (*Liebig's Annalen*, clxviii. 296). By methods similar to those already adopted by Landolt and Hilgard in the case of luminous flames (i. 1094), he has traced the gradual alteration in the composition of the mixture at different points in the internal area, viz., at 25 mm. and 50 mm. above the opening of the tube, and in the flame itself at a distance of 75 mm. above the tube. The flame was 120 mm. high, and the point of the inner zone was from 55 to 60 mm. from the end of the tube. The coal-gas, which varied but slightly in composition in the course of the observations, issued under a pressure of 12 mm., and was mixed with air in the tube in the proportion of 28.26 vols. of gas to 71.74 vols. of air, or slightly more than 2½ vols. of air to 1 of gas. The percentage composition of the gases drawn from the various points is given in the following table:

	Mixture in the tube 10 mm. below the opening	Above opening		
		25 mm.	50 mm.	75 mm.
H	13.74	9.68	4.84	2.80
CH ⁴	11.02	10.78	7.64	0.99
CO	0.80	0.58	2.99	2.21
C ² H ⁴	1.13	0.90	0.60	—
C ² H ²	0.85	0.66	0.44	—
O	14.88	13.85	6.92	—
N	56.47	59.58	61.66	66.66
CO ²	0.21	0.93	3.55	7.25
H ² O	0.90	3.14	13.66	20.20

From the percentage volume of nitrogen in the gaseous mixture, the proportion of admixed air and the contraction resulting from the combustion are readily calculated. The results thus arrived at are contained in the following table:

	In the tube	25 mm.	50 mm.	75 mm.	Complete combustion
Amount of air mixed with 100 vols. of gas	253.9	284.7	284.5	484.3	608.8
H	48.6	36.4	17.7	10.1	—
CH ⁴	39.0	40.1	28.0	5.7	—
CO	2.9	2.2	19.9	12.7	—
C ² H ⁴	4.0	3.4	2.2	—	—
C ² H ²	3.0	2.5	1.0	—	—
O	52.7	52.0	21.7	—	—
N	409.8	223.8	225.0	382.4	482.3
CO ²	0.8	3.5	13.0	41.7	62.4
H ² O	3.1	11.8	45.8	116.1	141.2
Contraction	353.9	375.7	369.8	574.7	685.9
		9.0	14.7	10.1	22.9

Of the two combustible gases of which coal-gas is chiefly composed, namely, marsh-gas and hydrogen, the hydrogen is the first to burn: the effect of this is seen in its diminished proportion in the gases at 25 mm. and 50 mm. above the tube. The cause of this rapid diminution in the proportion of the hydrogen, is to be ascribed mainly to the greater diffusive power of that gas, to its lower ignition-point, and to its greater rapidity of inflammation as compared with marsh-gas. It is known that a red-hot wire causes the combination of a mixture of oxygen and hydrogen, whereas it has no effect on a mixture of marsh-gas and oxygen. The rate of the combustion

of the hydrogen very rapidly diminishes as its proportion decreases, and that of the marsh-gas increases. At a height of 75 mm., that is, at about one-third of the distance between the top of the inner zone and the visible limit of the flame, the amount of the marsh-gas is only about one-third of that of the hydrogen. The increased ratio of the hydrogen is probably due to the high temperature of this part of the flame: the temperature of combustion of the marsh-gas in air is high enough to prevent the complete combustion of the hydrogen, or, what comes to the same thing, is sufficiently high to dissociate vapour of water already formed. To the large proportion of carbon monoxide present in the neighbourhood of the inner cone, is due the well-known reducing action of this portion of the flame.

In the combustion of the coal-gas a considerable contraction of volume occurs: 708.8 vols. of air and gas give only 685.9 vols. of combustion-products. On the whole, the rate of the contraction goes on increasing with the height of the flame, but at 75 mm. a sudden break in the continuity of the rate is manifest. This is owing to an increase in the volume of the still unburnt gas due to the decomposition and partial oxidation of the hydrocarbons: e.g., 1 vol. of ethene with 1 vol. of oxygen gives 2 vols. of carbon monoxide and 2 vols. of free hydrogen.

Blochmann has also analysed the gases present in the extreme outer edge of the flame: these, of course, consist of water-vapour and carbon dioxide mixed with oxygen and nitrogen.

The results are contained in the following table:

Height from burner, mm.	CO ^a	H ^a O	CO ^c	N	H ^a O CO ^a
10	3.30	14.36	8.29	74.05	4.35
20	3.49	14.95	7.95	73.61	4.29
30	4.07	14.68	8.31	72.94	3.63
40	3.95	12.90	8.94	74.21	3.27
50	3.64	11.22	10.03	75.11	3.08
60	3.02	11.02	9.72	75.34	2.81
70	4.35	10.82	9.20	75.63	2.49
80	4.91	10.73	8.92	75.44	2.18
90	5.38	10.72	8.60	75.30	1.99
100	5.73	10.81	7.76	75.70	1.89
110	6.58	10.97	6.61	75.84	1.67
120	7.18	11.14	6.17	75.51	1.55

These numbers also serve to indicate that the greater portion of the hydrogen present in the coal-gas is consumed in the lower parts of the flame. The greatest proportion of the water-vapour is formed in the lowest quarter of the flame; it then gradually decreases up to a height of about 90 mm., after which it slowly increases. On the other hand, the proportion of carbon dioxide suffers a pretty steady increase with the height of the flame.

The comparatively large proportion of burnt gases near the base of the flame, when connected with the facts that a space exists between the burner and the base of the flame, and that the inner and outer zones meet at that point, seems to indicate that a portion of the gas has time to form an explosive mixture with the external air, which ignites as a whole when its temperature is raised sufficiently high.

Blochmann, moreover, has determined the amount of the products of combustion in the atmosphere immediately surrounding the flame, drawn at a distance of 10 mm. from the edge. Below a distance of 20 or 25 mm. from the opening of the tube, not a trace of the products can be found: it is only at a height of about 30 mm. that these become perceptible. The ratios in the fourth column of the following table, afford additional proof that the free hydrogen burns proportionately faster than the hydrocarbons; at a height of 60 mm., and upwards, the ratio of water-vapour and carbon dioxide becomes constant, and almost identical with that given by the complete combustion of the gas, showing, therefore, that the marginal portions of the coal-gas are completely consumed.

Vertical height from opening of tube	H ² O Vapour	CO ²	H ² O / CO ²
20 mm.	0.06	0.00	—
30	0.77	0.16	4.8
40	1.14	0.40	2.8
50	1.73	0.63	2.7
60	1.90	0.75	2.5
70	2.42	1.05	2.3
80	3.71	1.37	2.7
90	2.40	0.91	2.6
100	2.70	1.10	2.4
110	2.90	1.13	2.6
120	2.7	1.30	2.1
100 vols. of gas give	137.79 vols.	62.62 vols.	2.3

The feeble luminosity of the Bunsen flame is due to a number of causes: (1) to a rapid oxidation of luminiferous material to gases of feeble illuminating power by the oxygen in the admixed air; (2) to the presence of diluting gases, which of themselves reduce the illuminating power; and (3) to the heat withdrawn by the indifferent gases, as nitrogen, and the products of combustion, carbon dioxide, and water. The loss of luminosity is not due to any one of these causes acting singly. A flame of mixed coal gas and air has a higher temperature than that of the undiluted coal gas, but it requires a still higher temperature in order that a separation of carbon shall occur.

When the volume of gas passing up the tube is small, there is great risk that the least draught of air, by interfering with the flow of the gas, or by mixing with it in sufficient amount to create an explosive mixture issuing at a less rate than that of its propagation of combustion, may cause the flame to retreat down the tube and burn at the bottom, with the production of disagreeably-smelling gases arising from imperfect combustion. The nature of the gases thus formed within the tube has been studied by Blochmann, whose results are seen in the following table (*Liebigs Annalen*, 173, 180):

	Gaseous mixture	
	Before the combustion	After the combustion
H.	10.91	9.14
CH ⁴	14.82	18.49
CO	2.26	4.64
C ² H ²	..	0.76
C ² H ⁴	1.57	0.63
C ² H ⁶	1.20	0.26
N.	46.54	46.54
O.	12.25	—
CO ²	0.45	3.02
H ² O	1.00	17.33
Contraction.	100.00	95.80
	..	4.20

When the flame burns at the bottom, a very much smaller quantity of air is into the tube: in the case cited, 58.9 vols. of air were mixed with 41.0 vols. of gas. On comparing the composition of the gas before burning with that remaining after partial combustion, it is seen that the proportion of marsh-gas is but very slightly diminished, whereas about half the hydrogen has disappeared, and with the decrease of the hydrogen there is a proportionate increase in the amount of water-vapour. The olefines have decreased, whereas the carbon monoxide is more than doubled in quantity and there is a certain amount of acetylene formed. To the carbon monoxide and acetylene is doubtless due the extremely disagreeable effect of the partially consumed gas (see also Thorpe, *Chem. Soc. J.* 1877, i. 627).

T. E. T.

FLAVOCOBAULT. See COBAULT AMMONIAS (p. 544).

FLAVOPURPURIN. See TRIOXYANTHRAQUINONES (p. 111).

FLAX. The fibres of New Zealand flax may be distinguished from those of ordinary flax and of hemp, by steeping the tissue under examination for a few hours in the aqueous solution of an aniline-dye, and washing it with water. The fibres of New Zealand flax are then found to be dyed a deep-red, while those of common flax, hemp, &c., remain white. This difference is particularly conspicuous after washing the stuff with soap-water (E. Fitzebert, *Bull. Soc. Chim.* [2], xxi. 545).

Testing.—To determine whether flour is spoiled or not, Wanklyn (*Pharm. J. Trans.* [3], iii. 827) exhausts it with cold water. Good flour contains but little dextrin or sugar, and consequently its aqueous extract when evaporated will leave but a very insignificant residue compared with that of spoiled flour, which contains a large quantity of these soluble substances. 100 parts of sound flour yield about 4·7 of extract, whereas spoiled flour yields from 12 to 18 pts.

The presence of bean-flour, or the flour of other leguminous seeds in wheat-flour, may be detected by mixing the flour with water to a thin paste, kneading it under water, leaving the starch to settle, then evaporating the liquid on the water-bath to a scum, and mixing the filtrate with acetic acid: legumin, if present, will then separate as a precipitate soluble in ammonia. Leguminous flour may also be recognised by microscopic observation, and by the much larger amount of ash which it yields when burnt (Droz, *N. Jahrb. Pharm.* xxxix. 3).

Detection and Estimation of Alum in Flour.—For quantitative estimation, Wanklyn (*loc. cit.*) uses at least 100 grams of flour; incinerates it in a stream of oxygen; and treats the ash, not with hydrochloric or nitric acid, but with a weighed quantity of strong sulphuric acid; heats the moistened mass till the sulphuric acid begins to evaporate; mixes it with a little water and a weighed quantity of caustic potash; and precipitates the alumina from the solution with ammonium chloride. The object of weighing the reagents is to take account of any small quantity of alumina that may be contained in them.

Wanklyn also points out that sulphuric acid always appears in the ash of flour, being formed during the incineration from the gluten, which contains about 1 per cent. of sulphur; and that consequently, for the detection of alum in flour and bread, it is of no use to determine the amount of sulphuric acid in the ash, the increase in the amount of this constituent caused by this adulteration being too small to yield any definite result. It is better to exhaust the flour with cold water, separate the gluten, and test for sulphuric acid in the filtrate (*Analyst*, i. 14).

The presence of alum in flour may also be detected by mixing 50 grams with 50 c.c. of water, 0·5 c.c. of logwood solution, and 5 c.c. of aqueous ammonium carbonate. If alum is present even in the proportion of 1 pt. in 10,000, the colour of the emulsion will be changed from pink to lavender-blue (J. C. Bell, *Analyst*, ii. 28). See also ALUMS (p. 67 of this volume).

On the Detection of Mineral Substances in Flour, see Vohl (*Deut. Chem. Ges. Ber.* ix. 1660; *Chem. Soc. J.* 1877, i. 753).

On Explosions in Flour-mills, see p. 767.

FLOWERS. The quantity of sugar contained in the petals of flowers has been determined by J. Boussingault (*Compt. rend.* lxxxiii. 978). The petals were carefully separated, and the soluble matter extracted by a given volume of water, the non-saccharine matter being eliminated by the addition of basic acetate of lead. In the following table, column I gives the percentage of dry matter in the petals (the leaves of these plants were also examined); column II gives the percentage of sugar (in the petals in their natural state) capable of reducing copper solution; column III the percentage of invertible sugar, reducing the copper solution only after treatment with acid.

	I	II	III
Lily petals . .	12·0	2·60	traces
„ leaves . .	16·0	2·75	traces
Oleander petals .	16·0	2·72	traces
„ leaves . .	26·5	2·46	traces
Portulacca flowers.	10·0	4·42	0·65
„ leaves . .	5·8	1·27	0·20
Acacia petals . .	13·0	3·80	0·00
Gum acacia petals	17·0	1·46	1·43
Rhododendron petals	8·0	2·20	0·60
Magnolia petals .	11·5	1·44	0·56
„ leaves . .	24·0	1·34	0·76

	I	II	III
Orange petals	21.0	5.00	0.60
„ whole flowers	22.0	4.11	0.94
„ leaves	28.0	traces	1.30
Snap-dragon petals	14.0	4.83	3.12
Lime flowers	25.0	0.54	0.27
„ leaves	33.0	1.08	1.91
Rose petals	13.0	3.40	traces

When exposed to the air after separation from the plant, the flowers lose their sugar, absorbing oxygen and exhaling carbon dioxide; but this action takes place only while they are in their normal state, and ceases entirely when they are dried.

FLUID CAVITIES IN MINERALS. W. N. Hartley (*Chem. Soc. J.* 1876, i. 137; ii. 237; 1877, i. 241) has examined the liquids enclosed in several minerals, especially quartz and topaz. The character by which the nature of these liquids can be most easily recognised is the 'critical point,' that is to say, the temperature at which the liquid is converted into vapour within the cavity, and disappears. To determine this temperature, a section of the mineral is immersed in water at various temperatures, and brought as quickly as possible under the microscope. In this manner many enclosed liquids were found to pass into vapour at 30.75°–31°, which, as shown by Andrews (*1st Suppl.* 402), is the critical point of carbon dioxide. In certain specimens of sapphire and topaz, the critical point was 2 or 3 degrees lower, which, as also appears from the experiments of Andrews, may be referred to the simultaneous presence of an uncondensable gas, most probably nitrogen, which was long ago recognised by Davy as occurring in mineral cavities. In quartz, on the contrary, Hartley has observed a raising of the critical point (as high as 33°), a result which may be attributed to the presence of a gas of lower tension at a given temperature. It cannot be ascribed to the presence of water, since at 31° and the high pressure which must exist within the cavity (that of carbon dioxide at 28.3° being upwards of 70 atmospheres), the tension of water-vapour is practically nothing. On the other hand, the raising of the critical point of carbon dioxide in these cases may be most probably attributed to the presence of hydrogen chloride, as this compound has been actually observed by Sorby and Hartley to occur in mineral cavities, and according to the experiments of Davy and Faraday it has in the liquid state at 10.6° a vapour-tension of 40 atmospheres, that of carbon dioxide at the same temperature being equal to 60 atmospheres.

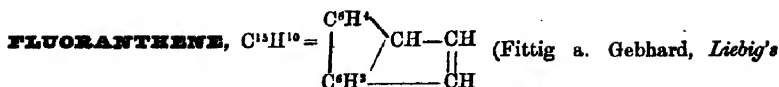
In topazes the enclosed liquid often consists of water. Supposing that topaz has been produced by the action of alkaline fluorides on kaolin, the non-occurrence of carbon dioxide in cavities of it quite full of liquid is easily explained. Some topazes contain cavities, one of which is completely filled with liquid carbon dioxide, while in another one-third of the space is filled with water, another third with liquid carbon dioxide, and the remainder with gaseous carbon dioxide, the space occupied by this gas having been left by the condensation of the aqueous vapour. In these cases it is supposed that the critical temperature of the water has not been attained, as otherwise the contents of neighbouring cavities would be similar.

Cavities in Rocks.—A large number of sections of granite and porphyry were examined, and in nearly all of them cavities were found containing water.

Gas-bubbles denser than Water.—When a mineral having cavities containing water together with a gas-bubble is heated, the bubble is observed to sink in the liquid, the gas, which is already under strong pressure, being further condensed by the vaporisation of the water, and so ultimately becoming denser than the water itself.

Crystal-shaped Cavities.—Cavities in crystals are often disposed symmetrically round the axis. A beryl, for example, exhibited cavities in the shape of tubes lying parallel to the six faces of the prism. In a hexagonal prism of quartz the cavities were of irregular shape, but so disposed round the principal axis that they were evidently caused by inclosures of water during successive growths of the crystal. Generally speaking, the cavities themselves are irregular in form and more or less rounded; especially is this the case in crystals artificially formed; but in certain cases the cavities are not only angular, but take the form of the crystals in which they are enclosed so exactly, that each side of each cavity is parallel to a face of the crystal. This is seen in quartz porphyry from Arran; in granite from the Mourne Mountains; in Aberdeen granite; in the granite from Tudyvan, Cornwall; and in quartz from Snowdon.

FLUOPORIC ACID (so-called). See BROWN (p. 346).



Annalen, cxciii, 142). This hydrocarbon, intermediate between phenanthrene ($\text{C}^{14}\text{H}^{10}$), and pyrene ($\text{C}^{16}\text{H}^{12}$), and related to fluorene ($\text{C}^{14}\text{H}^{10}$) in the same manner as phenanthrene to diphenyl, occurs, together with pyrene, in the solid hydrocarbons which separate from the last portions of the distillate obtained in boiling coal-tar down to coke. To separate it, the brownish-yellow press-cake containing these hydrocarbons is once recrystallised from alcohol, to separate the more soluble and greasy constituents, then redissolved in alcohol, and the solution is mixed with an alcoholic solution of picric acid, which throws down a very copious brownish-red precipitate, or if the solutions are somewhat concentrated, causes them to solidify completely to a crystalline pulp, consisting chiefly of pyrene-picric acid. The fluoranthene is also, for the most part, carried down in the form of a picric acid compound, unless the solution is very dilute, in which case the greater part of it remains in the liquid. To separate the two hydrocarbons, the precipitate is several times recrystallised from alcohol, and the more soluble crops of crystals, if their melting points are considerably lower than that of pyrene-picric acid, are collected apart. Further quantities of these lower-melting compounds are obtained by draining the liquid from the precipitate, and distilling off the greater part of the alcohol. These more soluble groups of crystals are then recrystallised from a rather large quantity of alcohol, till pyrene-picric acid no longer separates from the solutions, which are then decomposed by ammonia. The hydrocarbon thus obtained (m. p. 113° – 115°) still, however, contains a small quantity of pyrene. A similar mixture, poor in pyrene, is obtained when pyrene-picric acid, purified as completely as possible by repeated crystallisation from alcohol, is decomposed by ammonia, and the precipitated pyrene crystallised from a large quantity of alcohol. The first crops of crystals then consist of pure pyrene, but the last mother-liquors yield large shining laminae (m. p. 115°), consisting of a mixture of pyrene and fluoranthene. For further purification, the mixture of the two hydrocarbons is freed as far as possible from pyrene by recrystallisation, then recombined with picric acid, the resulting compound again subjected to frictional crystallisation, &c.; and by this somewhat tedious process a picric acid compound is at length obtained, which melts at 182° – 183° , and is much lighter coloured than the pyrene-picric acid which does not melt below 222° . From this compound the hydrocarbon is separated by ammonia, and finally purified by crystallisation from boiling alcohol.

Fluoranthene has also been separated by Goldschmidt (who calls it *idryl*) together with anthracene, phenanthrene, chrysene, and pyrene, from a product obtained in the distillation of Idrian quicksilver ores (*Dent. Chem. Ges. Ber.* x. 2022).

Fluoranthene is sparingly soluble in cold alcohol, easily in boiling alcohol, also in ether, carbon sulphide and glacial acetic acid. From a concentrated alcoholic solution it separates in cooling in long thin needles; from a very dilute solution in large thin, very brilliant, colourless, monoclinic tablets, exhibiting the combination $OP : +P\infty : \infty P$, and much elongated in the direction of the axis of symmetry. Axes $a : b : c = 1.496 : 1 : 1.025$. Angle $ac = 82^{\circ} 50'$; $\infty P\infty : P = 68^{\circ} : \infty P : OP = 86^{\circ}$; $+P\infty : OP = 36\frac{1}{2}^{\circ}$. Cleavage perfect parallel to OP . Plane of optic axes parallel to the plane of symmetry. First median line almost exactly at right angles to OP . Strong double refraction. Melting point 109° (Fittig a. Gebhard); 110° (Goldschmidt).

Fluoranthene-picric acid, $\text{C}^{14}\text{H}^{10} \cdot \text{C}^6\text{H}_3(\text{NO}_2)_3\text{O}$, separates from a mixture of the hot alcoholic solutions of fluoranthene and picric acid (equal weights) in long shining needles, having a reddish-yellow colour, much lighter than the picric compounds of the other hydrocarbons of the group. It melts at 182° – 183° (F. and G.); 184° (Goldschmidt): is slightly soluble in cold, more easily in hot alcohol, and may be recrystallised from alcohol without alteration, but is decomposed by boiling with water, and still more easily by drenching with ammonia, the hydrocarbon being set free.

Dibromofluoranthene, $\text{C}^{14}\text{H}_8\text{Br}_2$.—When bromine in excess is added by drops to a cold solution of fluoranthene in carbon sulphide, a brisk evolution of hydrobromic acid takes place, and a yellow crystalline precipitate is formed, consisting chiefly of dibromofluoranthene, and easily purified by boiling with alcohol and recrystallising the residue from boiling carbon sulphide. Dibromofluoranthene crystallises from this solvent in light yellowish-green shining needles, melting at 204° – 205° , very sparingly soluble in alcohol, ether, and glacial acetic acid; more easily, but by no means freely, in boiling carbon sulphide.

Together with this dibromo-compound, there are also formed other bromofluoranthenes which may partly be extracted from the product of the reaction by boiling

alcohol, partly remaining in the mother-liquor of the recrystallisation; they have not been obtained pure.

Trinitrofluoranthene, $C^{12}H^7(NO_2)^3$.—Fluoranthene, added by small portions to fuming nitric acid, dissolves readily with rise of temperature, and a nitro-compound separates after a few seconds; and if, after the whole of the hydrocarbon has been added, the liquid be heated till the whole is dissolved, and then left to cool, the trinitro-compound separates abundantly in small needles, which are nearly insoluble in all the ordinary solvents, and must be washed on a platinum funnel with strong nitric acid.

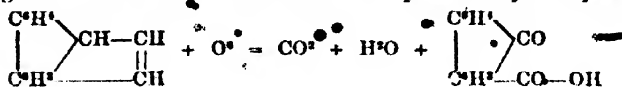
Trinitrofluoranthene crystallises from hot nitric acid, in which it is moderately soluble, in shining yellow needles which do not melt at 300° . It dissolves but very sparingly in alcohol, ether, carbon sulphide, and glacial acetic acid, even at the boiling heats of these liquids.

Oxidation-products of Fluoranthene.—Fluoranthene reacts with oxidising agents like phenanthrene, being readily oxidised, both on addition of chromic anhydride to its solution in glacial acetic acid, and by boiling it with potassium dichromate and dilute sulphuric acid, yielding in either case a quinone and an acid which are easily separated one from the other. The latter method is to be preferred, as it effects a more gradual and complete oxidation. The products float on the liquid in the form of a brownish coagulated mass, which may be filtered off after cooling, washed with water, then pulverised and repeatedly lixiviated with sodium carbonate.

Fluoranthene-quinone, $C^{12}H^6O_2$, is found, together with unaltered fluoranthene, and difficultly soluble chromic compounds, in the residue left after treating the mass above mentioned with sodium carbonate. The quinone and the hydrocarbon may be dissolved out by boiling alcohol, and separated from one another by treatment with acid sodium sulphite, which dissolves the quinone with moderate facility; and the solution, on addition of hydrochloric acid, deposits nearly colourless needles, apparently consisting of the hydroquinone, as they burn in the air, and are converted in great part during recrystallisation from alcohol, easily and completely on treatment with ferric chloride, into the quinone. The latter crystallises from alcohol in small red needles, melting at 187° – 188° (F. and G.), 189° (Goldschmidt); moderately soluble in alcohol and in glacial acetic acid.

Diphenylene-ketone-carbonic acid, $C^{14}H^6O^3 = \begin{array}{c} C^6H^4 \\ \diagup \quad \diagdown \\ CO \quad CO \\ \diagdown \quad \diagup \\ C^6H^4 \end{array}$. This acid

constitutes by far the greater part of the product of the oxidation of fluoranthene by chromic acid mixture; it may be dissolved out by sodium carbonate, and thrown down therefrom by hydrochloric acid, as a bulky reddish precipitate. A small additional quantity may be obtained from the portion of the crude product insoluble in sodium carbonate, by decomposing the chromium-compounds which remain undissolved on treatment with alcohol, with boiling hydrochloric acid, dissolving the portion which then remains behind in sodium carbonate, and precipitating with hydrochloric acid. The acid may be obtained quite pure by converting it into its barium salt, which crystallises well, separating it therefrom by hydrochloric acid, and crystallising from dilute alcohol. Its formation is represented by the equation

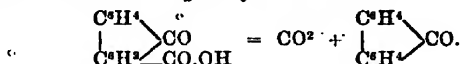


Diphenylene-ketone-carbonic acid is nearly insoluble in cold water, slightly soluble in boiling water, easily in alcohol and ether, and crystallises in orange-red needles an inch long, melting at 191° – 192° . It has the same percentage composition as oxyanthraquinone, but has no further connection with that compound, being in fact a true acid, which dissolves with the utmost ease in alkalis and alkaline carbonates, and expels carbonic acid even from insoluble carbonates. It is monobasic. Its **barium salt**, $(C^{14}H^6O^3)^2Ba + 4H^2O$, easily obtained by boiling the acid with water and barium carbonate, is sparingly soluble in cold, somewhat more easily in hot water, and crystallises from the dilute solution in very bulky groups of slender, silky, faintly coloured needles, which in the air-dried state contain 4 mols. water of crystallisation. The **calcium salt**, $(C^{14}H^6O^3)^2Ca + 2H^2O$, prepared like the barium salt, separates from the aqueous solution during evaporation in small yellow needles, not much more soluble in hot than in cold water. The **silver salt**, $C^{14}H^6O^3Ag$, separates on adding silver nitrate to the solution of either of the preceding salts, as a faintly yellowish-green flocculent precipitate very slightly soluble in water.

Diphenylene-ketone-carbonic acid unites directly with 1 mol. KOH, forming the

potassium salt, $\begin{array}{c} \text{C}^6\text{H}^4-\text{CO}^2\text{K} \\ | \\ \text{C}^6\text{H}^4-\text{CO}^2\text{K} \end{array}$, of an acid isomeric with diphenic acid (p. 658). See
ISODIPHENIC ACID.

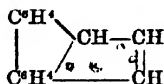
The constitution of diphenyleneketone-carbonic acid is determined by the mode of its decomposition, when heated alone, and with zinc-dust. In the former case, about one-tenth of the acid volatilises unaltered, and the rest is resolved almost quantitatively into carbon dioxide and diphenylene-ketone:



The same decomposition takes place when the acid is heated with lime, but it requires a higher temperature and is less complete. The same products are also formed in the first instance when the acid is heated with *zinc-dust*, but the diphenylene-

ketone is then reduced to diphenylene-methane or fluorene, $\begin{array}{c} \text{C}^6\text{H}^4 \\ \diagup \quad \diagdown \\ \text{C}^6\text{H}^4 \end{array} \text{CH}^2$.

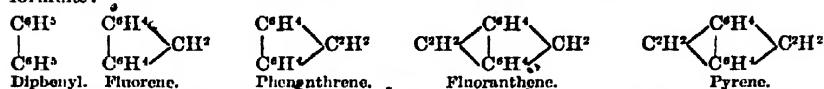
The formula thus established for diphenyleneketone-carbonic acid shows that fluoranthene, by the oxidation of which it is produced, must be represented by the formula



and that it is related to fluorene, in the same way as phenanthrene is to diphenyl, differing, that is, from fluorene by 2 atoms of carbon, or being derived from it by substitution of the bivalent radicle, C^2H^2 or $-\text{CH}=\text{CH}-$, for 2 atoms of hydrogen.

With respect to the orientation of the group $\text{CH}=\text{CH}$, in phenanthrene and fluoranthene, it has lately been shown by Schmitz (*Liebig's Annalen*, xciii. 115) that diphenylene-ketone is converted by fusion with potash into phenyl-benzoic acid, $\text{C}^6\text{H}^4.\text{C}^6\text{H}^4.\text{COOH}$ (q.v.), and that this acid is scarcely attacked by comparatively weak oxidising agents, such as dilute nitric acid or permanganates, but is completely oxidised by chromic acid mixture to carbonic acid and water. Now this behaviour is known to be characteristic of ortho-derivatives, and hence it may be inferred as very probable that in phenyl-benzoic acid, the group CO^2H is in the ortho-position relatively to the point of junction of the two benzene-nuclei, and that consequently a similar position must be occupied by the group $\text{CH}=\text{CH}$ in phenanthrene and fluoranthene.

Atterberg (*Deut. Chem. Ges. Ber.* xi. 1224) proposes to represent the hydrocarbons derived from diphenyl by successive addition of 1 at. carbon-atom, by the following formulæ:



FLUORENE or **DIPHENYLENE-METHANE**, $\text{C}^{14}\text{H}^{10} = \text{C}^6\text{H}^4.\text{CH}^2.\text{C}^6\text{H}^4$. This hydrocarbon has already been described under diphenylene-compounds (p. 671), where it is stated that the fluorene from coal-tar discovered by Berthelot, and further studied by Barbier, agrees in most of its properties with the diphenylene-methane obtained by Fittig from diphenylene-ketone, and by Gräbe from diphenyl-methane, but differs from it in yielding by oxidation a quinone as well as a ketone, and in the crystalline form and melting point of its dibromo-derivative. Quite recently, however, the diphenylene-methane prepared from diphenylene-ketone has been re-examined by Fittig & Schmitz (*Liebig's Annalen*, xciii. 134, July 1878), who have obtained it in greater purity than before, and shown that it agrees in every respect with coal-tar fluorene, with the exception of slight differences in physical properties which may be fairly attributed to the presence of small quantities of other hydrocarbons in the latter, seeing that it is not obtained by any definite reaction, but separated from a mixture of hydrocarbons by fractionation.

To prepare pure diphenylene-methane, an intimate mixture of diphenylene-ketone and zinc-dust was introduced into a combustion-tube, then a layer of zinc-dust alone; the open end of the tube was bent downwards; and the tube was strongly heated in a combustion-furnace. Diphenylene-methane then distilled over in the form of a colourless oil, which solidified in the downward-bent worm of the tube, accompanied by a red substance apparently the same as that which is formed as a bye-product in

the preparation of diphenylene-ketone. The quantity of this red body formed increases as the temperature is raised; but nevertheless it is best to employ a strong heat, as at lower temperatures unaltered diphenylene-ketone distils over, which is more difficult to separate than the red substance. The diphenylene-methane may, in fact, be separated from the latter by a single distillation, and obtained quite pure by recrystallisation from alcohol.

The hydrocarbon thus prepared crystallises from alcohol in shining, perfectly colourless laminae which, whether in the dry state or in alcoholic solution, exhibit only a faint bluish fluorescence. The strong fluorescence observed by Berthelot & Barbier in coal-tar fluorene (hence the name) was probably due to the admixture of other hydrocarbons. Diphenylene-methane dissolves sparingly in cold, easily in hot alcohol, also in ether, benzene, and carbon sulphide. It melts between 112° and 113° , and boils at 294° – 295° (thermometer up to 219° wholly in the vapour), which is considerably below the boiling point of diphenylene-methane given by Graebe (300° – 305°) and of coal-tar fluorene by Barbier (305°).

The *picric acid compound*, $C^{12}H^{10}.C^6H^3(NO^2)_3O$, prepared by mixing the ethereal solutions of its components in the calculated proportion crystallises by spontaneous evaporation in red-brown compact prisms, melting at 79° – 80° (80° – 82° Barbier).

Dibromodiphenylene-methane, $C^{12}H^8Br^2$, is prepared by adding 2 mols. bromine to 1 mol. of the hydrocarbon dissolved in carbon sulphide. On distilling off the solvent, after the evolution of the hydrobromic acid has ceased, washing the residue with ether, dissolving it in carbon sulphide, and leaving the solution to evaporate, the compound separates in well-defined tabular crystals, perfectly transparent and colourless, and giving by analysis numbers agreeing exactly with the formula. It melts at 162° – 167° (at 163° – 164° Graebe, 166° – 167° Barbier).

The crystals, examined by Arzruni, are perfectly limpid monoclinic prisms, $\infty P : R \infty : OP$, frequently with addition of $\infty R \infty$; tabular; cleaving perfectly parallel to OP , somewhat less distinctly parallel to $\infty P \infty$. Axes $a : b : c = 0.6626 : 1 : 0.6974$. Angle $ac = 78^{\circ} 21'$; $\infty P : \infty P = 57^{\circ} 42'$; $\infty P : OP = 79^{\circ} 48' 30''$; $R \infty : OP = 34^{\circ} 20'$. The plane of the optic axes is parallel to the plane of symmetry; the first median line lies in that plane, and the second coincides with the axis of symmetry. These crystals are evidently different from those of the dibromo-derivative of Barbier's fluorene, the measurements of which, by Bouchardat (p. 61), have been tested by Arzruni, and found to be quite exact. Fittig & Schmitz, however, having obtained some of these crystals from Barbier, dissolved them in carbon sulphide, and left the solution to evaporate, whereupon it first deposited the colourless crystals above described, and the mother-liquor, which was somewhat strongly coloured, deposited, on further evaporation, large yellow crystals, the measurements of which agreed exactly with those of Barbier's crystals. The mother-liquor of these yielded a second crop of the colourless crystals, which were again succeeded by the yellow crystals, and so on. Hence it appears that dibromo-diphenylene-methane is dimorphous. Moreover, as the colourless solution of the compound prepared by Fittig & Schmitz never deposits the yellow crystals, whereas Barbier's crystals are always coloured and separate from a coloured solution, it is most probable that the crystallisation of the compound in this form is due to the presence of a small quantity of some other hydrocarbon.

Dinitro-diphenyl-methane, $C^{12}H_8(NO^2)_2$, prepared, according to Barbier's directions, by adding the hydrocarbon to a mixture of equal volumes of fuming nitric acid and glacial acetic acid, pouring the product, after twelve hours' standing, into water, and dissolving the resulting precipitate in glacial acetic acid, crystallises therefrom in colourless needles melting at 199° – 201° , and very slightly soluble in boiling alcohol, from which it separates in long shining spicules. Barbier describes this compound as crystallising in reddish needles, very slightly soluble in all the ordinary solvents, crystallisable only from a mixture of nitrobenzene and light petroleum oils, and melting, with decomposition, at a temperature above 260° ; this product was doubtless impure.

Oxidation-products of Diphenylene-methane.—When 2 pts. of crystallised chromic anhydride were added to 1 pt. of diphenylene-methane dissolved in alcohol, the solution on cooling deposited, first the unaltered hydrocarbon, then a considerable quantity of diphenylene-ketone, but not a trace of the quinone which, according to Barbier, is formed at the same time. Hence Fittig & Schmitz conclude that, if Barbier did really obtain a quinone, it must have been formed, not from diphenylene-methane, but from some other hydrocarbon* contained in his fluorene.

* Most probably another modification of diphenylene-methane. The same supposition may also account for the fact that coal-tar fluorene yields two modifications of dibromodiphenylene-methane, whereas the hydrocarbon prepared by reduction of diphenylene-ketone, which is homogeneous, yields only one.

Rosærcin-phthalein. See PHTHALEINS.

See LIGHT.

1. *Metallic*.—The sp. gr. of *lithium fluoride* is 2.295 at 21.58°; of *sodium fluoride*, 2.588 at 14.5°; of *potassium fluoride*, 2.096 at 21.5°. The sp. gr. of *rubidium fluoride*, determined on a very small quantity of material, is 3.102 at 17°. This salt is extremely deliquescent.

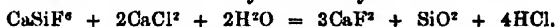
When *silver fluoride* is added to gold chloride, a pale-brown precipitate falls, which is a mixture of silver chloride and gold oxide: $2\text{AuCl}_3 + \text{AgF} + 3\text{H}_2\text{O} = \text{Au}_2\text{O}_3 + 4\text{AgCl} + 4\text{HF}$. A similar result is obtained with platinum (F. W. Clarke, *Sill. Am. J.* [2], xiii. 291).

Barium Fluoride, BaF_2 , may be crystallised in cubes (with edges 0.02 mm. long) from solution in water; also by heating the precipitated fluoride to 240° with water containing nitric acid. With water containing hydrochloric acid, prismatic crystals are obtained, probably a double salt of BaF_2 and BaCl_2 (Scheerer a. Drechsel, *J. pr. Chem.* [2], vii. 63).

Calcium Fluoride. Crystals of fluorspar from the Münsterthal and other localities in Baden, have been examined by F. Klocke (*Jahrb. f. Min.* 1874, 731), who has observed the new forms 8O_2 and 8O_4 . A. v. Lasaulx (*ibid.* 75, 134) describes the triakisoctohedron 4O , as an independent form of fluorspar from Striegau in Silesia.

Artificial Crystallisation.—When pulverised fluorspar, or amorphous calcium fluoride obtained by precipitation, is fused in a platinum crucible with chloride of calcium, potassium, or sodium, and the fused mass is left to cool very slowly, crystallised calcium fluoride is obtained, which may be separated from the soluble salts by boiling with water. It then remains in the form of regular octohedral crystals, a few of which are isolated and perfectly formed, while the greater number are joined end to end, forming rectangular branches; but the cubic form, which is that of natural fluorspar, is not obtained in this way, either alone or in combination with the octohedron.

Such forms may, however, be produced by operating in the wet way, namely, by heating neutral calcium silicofluoride with solution of calcium chloride for several hours at 250° in a sealed glass tube. The tube is then found to be lined with microscopic crystals of calcium fluoride, having the form of octohedrons more or less modified with cubical faces. The reaction by which they are formed is:



Lastly, calcium fluoride may be obtained in octohedral crystals, without any cubic modifications, by heating the amorphous fluoride with water slightly acidulated with hydrochloric acid, in a sealed tube to 240° for ten hours.

Mixtures of *calcium sulphate* and *barium fluoride*, either fused with a mixture of potassium and sodium chloride or heated with water to 240°, yielded, not separate crystals of barium sulphate and calcium fluoride, but a chemical compound of the two, crystallised in prisms. Separate crystals of the two salts were, however, obtained by filling the bend of a U-tube with water, and placing in one of its arms a loose plug of filter-paper containing gypsum, and in the other a similar plug containing barium fluoride, each plug dipping into the water, so as to effect a gradual dissolution of the two salts, and bring them very slowly together in the state of very dilute solutions. After this slow action had gone on for several weeks, barium sulphate was found deposited in tubular and wedge-shaped crystals, and calcium fluoride in sharp-edged cubes mostly implanted on the crystals of barium sulphate (Scheerer a. Drechsel, *J. pr. Chem.* vii. 63).

On Etched Figures on Fluorspar, see Baumhauer (*Jahrb. f. Min.* 1876, 692; *Chem. Soc. Jour.* 1877, ii. 116).

On a Fluid Cavity in Fluorspar, see Mallet (*Chem. Soc. Jour.* 1877, ii. 144).

On the Use of Fluorspar and other Fluorides in Glass-making, see GLASS.

Glucinum Fluorides. Double fluorides of glucinum and the alkali-metals are described by Marignac (*Ann. Chim. Phys.* [4], xxx. 45). With *potassium fluoride* two salts are obtained, viz. $\text{GF}_2 \cdot 2\text{KF}$ and $\text{GF}_2 \cdot \text{KF}$. The former is easily obtained in laminar crystals by leaving a mixed solution of the two salts in the calculated proportion to evaporate slowly; the latter separates in warty crystalline crusts on mixing the solution of the former with excess of glucinum fluoride, and leaving it to evaporate. With *sodium fluoride*, the two salts, $\text{GF}_2 \cdot 2\text{NaF}$ and $\text{GF}_2 \cdot \text{NaF}$, are obtained, the first of which crystallises in two different forms. The second, which has only approximately the composition indicated by the formula, forms warty crusts. The ammonium salt, $\text{GF}_2 \cdot 2\text{NH}_4\text{F}$, is isomorphous with the corresponding potassium salt.

Magnesium Fluoride, MgF_2 . On adding a solution of an alkaline fluoride to one of magnesium sulphate, an amorphous gelatinous precipitate of magnesium fluoride

is obtained, which stops the filter and is difficult to wash. A better process is to treat pure magnesia with pure hydrofluoric acid, and remove the excess of the latter by heating the product to 100°. The precipitate thus obtained is perfectly amorphous, but on heating it to the melting point of cast-iron, it fuses completely, and on cooling solidifies to a crystalline mass made up of small prisms. Somewhat larger tabular crystals may be obtained by fusing a mixture of the amorphous fluoride with an alkaline chloride, and removing the latter by treatment with water when the mixture has become cold. The crystals thus formed are twins, and when examined by polarised light exhibit the same characters as those from the fused magnesium chloride. They have been measured by Struener, who pronounces them to be identical with the native fluoride, sellaite. The crystals have a density of 2.856 at 12°; hardness = 6. After being submitted to the influence of an electric current from a Ruhmkorff's coil for a short time, and then gently heated, they become fluorescent in the same way that fluor spar does, emitting a violet light. Sellaite itself exhibits a similar property, as do also other crystalline fluorides, but neither calcium nor magnesium fluoride in the amorphous state is capable of being rendered fluorescent.

Crystalline magnesium fluoride melts at a very high temperature. It is insoluble in acids, with exception of concentrated sulphuric acid, which readily decomposes it. With calcium, barium, and strontium sulphates it forms readily fusible compounds of definite composition. Heated with aluminium sulphate, it yields aluminium fluoride (A. Cossa, *Gazz. chim. ital.* vii. 212).

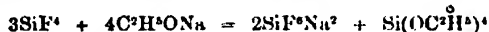
Nickel Fluoride, $\text{NiF}_2 \cdot 3\text{H}_2\text{O}$, is prepared by dissolving nickel hydrate in aqueous hydrofluoric acid. On concentrating the solution, a granular mass of crystals separates out. The last portions of water are retained at 130°. Sp. gr. 2.014 at 19°. The anhydrous fluoride has the sp. gr. 2.855 at 14°; molecular volume, 13.65.

When solutions of nickel and silver fluorides are mixed together and concentrated, the nickel salt usually separates out alone, the silver salt apparently decomposing. In one instance, however, pale apple-green needles, mixed with rhombohedrons, were obtained, which analysis showed to be a highly hydrated double fluoride of nickel and silver (Clarke, *Sill. Am. J.* [2], xiii. 291).

Zinc Fluoride. The sp. gr. of the hydrated salt is 2.567 at 10° and 2.535 at 12°; of the anhydrous salt, 2.666 at 17° and 2.612 at 12° (Clarke).

2. *Non-metallic.* **Phosphorus Fluoride**, PF_3 . This compound, described by Davy and by Dumas as a very volatile liquid (iv. 522), is, according to Macivor, (*Chem. News*, xxxii. 258), gaseous at ordinary temperature and pressure.

Silicon Fluoride. By the action of this compound on sodium ethylate, ethyl silicate is produced:



(Klippert, *Deut. Chem. Ges. Ber.* viii. 713).

Silicofluorides. The *ferrous salt*, $\text{SiF}_4 \cdot \text{Fe} + 6\frac{1}{2}\text{H}_2\text{O}$, is obtained by digesting iron filings at a gentle heat in silicofluoric acid, dissolving the resulting mass in water containing a few drops of the acid, and evaporating the solution on the water-bath. It forms large bluish-grey hexagonal crystals, and in the state of powder has a density of 1.981 at 17.5°; 1 pt. of the salt dissolves in 0.78 pt. of water at 17.5°; in hot water it is somewhat less soluble. The crystals oxidise in moist air.

The *cobalt salt*, $\text{SiF}_4 \cdot \text{Co} + 6\frac{1}{2}\text{H}_2\text{O}$, may be prepared by dissolving cobalt carbonate in silicofluoric acid, or by acting on barium silicofluoride with a boiling solution of cobalt sulphate. It forms large red hexagonal crystals, which effloresce very slightly in dry air. In the state of powder it has a density of 2.113-2.121 at 19°. One part of the crystals dissolves in 0.847 pt. water at 21.5°. The salt is somewhat more soluble in hot water than in cold water (F. Stolba, *Chem. Centr.* 1876, 16).

On the preparation of Sodium Silicofluoride and its use in Volumetric Analysis, see Stolba (*Zeitschr. anal. Chem.* xi. 199; *Chem. Soc. Jour.* 1873, 406).

FORESITE. A zeolite, occurring together with desmin and stilbite, in druses of the tourmaline-granite of Elba. It forms rhombic crystals, exhibiting the faces $\infty P \infty$, $\infty P \infty$, OP, and less frequently P, and, so far as can be decided by imperfect measurement, appears to be isomorphous with desmin. Sp. gr. = 2.403 to 2.407°. The analytical numbers (A) agree nearly with the values (B) calculated from the formula $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 8\text{Al}_2\text{O}_3 \cdot 24\text{SiO}_2 \cdot 24\text{H}_2\text{O}$:

	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	H_2O
A.	49.96	27.40	5.47	0.40	0.77	1.38	15.07 = 100.45
B.	49.27	28.14	5.76	—	—	2.05	14.78 = 100

(G. vom Rath, *Pogg. Ann. clii.* 31).

FOREST TREES.—Under this head an attempt will be made to bring together the various researches on the Chemistry of the Forest. It will be impossible to describe the many different bodies which have been found as constituents of trees; an account of these must be sought for under their respective names; the aim will rather be, to show the general composition of the different parts of trees, and the relation of this composition to the processes of life and growth. We shall consider—1. The Trunk and Branches: 2. The Sap: 3. The Leaf: 4. The Blossom, Fruit, and Seed: 5. The Forest Litter: 6. The Annual Requirements of a Forest.

As a good deal of confusion prevails respecting the names of certain trees, it will be well to state at starting that the English names of the principal trees referred to have the following Latin and German equivalents:

Beech	<i>Fagus sylvatica</i>	Buche, Rothbuche
Hornbeam	<i>Carpinus Betulus</i>	Hainbuche, Weissbuche
Birch	<i>Betula alba</i>	Birke
Maple	<i>Acer platanoides</i>	Ahorn
Horsechestnut	<i>Æsculus Hippocastanum</i>	Roskastanie
Larch	<i>Abies Larix</i>	Lärche
Spruce fir	<i>Abies excelsa</i>	Fichte
Silver fir	<i>Abies Picea</i>	Weisstanne
Scotch pine	<i>Pinus sylvestris</i>	Kiefer

1. THE TRUNK AND BRANCHES.

The proportion of water in a tree increases from below upwards, is greater in the branches than in the trunk, and greater in the small branches than in the larger ones. Schroeder (*Tharander forstliches Jahrbuch*, 1874, 280) found the distribution of water in a spruce fir felled on May 20 to be as follows:

Trunk with bark 36.15 per cent.	Branches over 1 c.m. diam. 47.95 per cent.
Thin end of trunk 50.80 per cent.	Branches under 1 c.m. diam. 51.56 per cent.
Leaves 52.49 per cent.	

According to Gelesnoff (*Jahresb. Agri. Chem.* 1873-4, i. 268), the percentage of water, after increasing from below upwards, diminishes again at the summit of the trunk. Stöckhardt (*ibid.* 1864, 81) determined the water in beech and larch at three heights in the trunk, operating on trees felled every month during a year; the percentages found in wood and bark were as follows:

	Lower	Middle	Upper		Lower	Middle	Upper
Beech bark:				Larch bark:			
Winter . . .	40.5	41.5	39.3	Winter . . .	36.4	45.1	51.6
Spring . . .	43.7	42.8	47.0	Spring . . .	37.3	51.9	53.8
Summer . . .	42.1	44.1	48.3	Summer . . .	38.4	49.2	41.6
Autumn . . .	39.0	40.1	40.1	Autumn . . .	36.0	41.5	47.6
Beech wood:				Larch wood:			
Winter . . .	42.1	47.4	45.6	Winter . . .	39.5	45.7	50.0
Spring . . .	37.9	40.7	43.5	Spring . . .	43.2	45.0	48.4
Summer . . .	37.4	43.7	47.1	Summer . . .	37.9	39.0	46.0
Autumn . . .	40.3	43.5	45.9	Autumn . . .	38.9	43.5	52.9

Beech wood is seen to contain its maximum of water in the winter months; in the spring (March to May), the water in the wood rapidly falls to a minimum, while at the same time the percentage of water in the bark rises, reaching its maximum in summer. During the growing months the bark contains more water than the wood; during the resting months the reverse is the case. The same general principle is seen in the results with larch.

T. Hartig (*Jahresb. agri. Chem.* 1868-9, 231), from determinations made on borings 4 ft. from the ground, states that the minimum contents in water occurs in autumn before the fall of the leaf. The maximum is in winter in the case of the fir tribe; with other trees in winter or spring. With trees bleeding when bored in spring, the maximum is at the bleeding period. Gelesnoff determined the water in entire trees every month for a year. Scotch pine gave a maximum (January) of 64.6 per cent., and a minimum (May) of 55.3 per cent.; mean for the year 61.1 per cent. Aspen gave a maximum (March) of 56.6 per cent., and a minimum (May) of 48.9 per cent.; mean for the year 52.8 per cent. Birch gave a maximum (May) of 65.9 per cent., and a minimum (December) of 43.5 per cent.; mean for the year 49.2 per cent. Maple gave a maximum (April) of 45.8 per cent., and a minimum (January) of 38.6 per cent.; mean for the year 42.1 per cent. Hartig noticed a con-

siderable diurnal variation during fine warm weather, the percentage of water in the trunk being much less between 2 and 3 p.m. than at sunrise.

A rapidly growing tree will contain much more water than a tree of the same species which has grown slowly.

The tissues of a tree are made up of cellulose, more or less incrusting with lignose, frequently also with calcium salts and silica. The older portions of the wood, and the epidermis, are the parts containing most incrusting matter. Different kinds of wood contain very different proportions of incrusting matter, the hardest and heaviest woods generally containing most. Hugo Müller (*Die Pflanzensaser*, 160) has determined the proportion of cellulose and incrusting matter in various woods. After successive extraction with water, and with a mixture of alcohol and benzene, the incrusting matter was removed by repeated treatment, first with bromine water, and then by boiling with dilute ammonia; the residual cellulose was then weighed. The percentage results obtained were as follows:

	Water	Soluble in water	Soluble in alcohol and benzene	Cellulose	Incrusting matter	Incrusting matter for 100 cellulose
Black Poplar	12.10	2.88	1.37	62.77	20.88	33.3
Silver Fir	13.87	1.26	0.97	56.99	26.01	47.2
Birch	12.48	2.65	1.14	55.52	28.21	50.8
Willow	11.66	2.65	1.23	55.72	28.74	51.6
Scotch Pine	12.87	2.05	1.63	53.27	28.18	52.9
Chestnut	12.03	5.41	1.10	52.64	28.82	54.7
Linden	10.10	3.56	3.93	53.09	29.32	55.2
Mahogany	12.39	9.91	1.02	49.07	27.61	56.3
Alder	10.70	2.48	0.87	51.62	31.33	57.3
Boxwood	12.90	2.63	0.63	48.14	35.70	74.2
Beech	12.57	2.41	0.41	45.47	39.14	86.1
Oak	13.12	12.20	0.91	39.47	34.30	86.9
Teak	11.35	7.93	3.74	43.12	38.16	88.5
Lignum Vitæ	10.88	6.06	15.63	32.22	35.21	109.2
Ebony	9.40	9.99	2.54	20.99	48.08	160.3

Only woods rich in cellulose are suitable as material for making paper.

Starch is a nearly constant ingredient of the stems of trees, and forms the chief bulk of the reserve matter out of which leaves and shoots are produced in spring. The deposition of starch commences early in summer, and is completed at the fall of the leaf. The tissues characteristically rich in starch are the parenchyma of the bark, the pith-rays, the pith, and in some cases the parenchyma of the wood. The tissues of the root are frequently rich in starch. In different trees the distribution of starch will vary, one description of tissue being richer in some trees than in others. In a section of oak, felled in winter, the arrangement of the starch may be plainly seen by moistening with solution of iodine.

The sugar in spruce fir wood has been determined by Ulbricht (*Tharandter forst. Jahrbuch*, 1874, 183). Two trees were felled every month during a year, and the trunk wood analysed. 1,000 of dry wood contained the following proportions of sugar:

Sap wood

Winter	0.32	0.10	0.27
Spring	1.30	0.53	0.85
Summer	0.49	0.34	0.43
Autumn	0.40	0.11	0.25

The sap wood clearly contains a much larger proportion of sugar than the heart wood. The sugar reaches its maximum in spring, when the reserve starch is undergoing solution.

Tannin is, with few exceptions, another general ingredient of forest trees. It is apparently related to starch, and may be formed from starch, or converted into it, at different stages of vegetation. Tannin occurs in those parts of a tree which are also characteristically rich in starch, as for example the inner layers of the bark. It is also frequently abundant in young shoots and buds, in the husks of fruit, and in various forms of epidermis. The proportion of tannin is generally greatest during

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winter or spring, and diminish considerably in the summer months. Stöckhardt (*Jahresb. Agri. Chem.* 1864, 78) determined the amount of tannin in beech and larch bark during every month for a year; the following table gives a summary view of the percentages of tannin found in the dry bark:

Per cent. Tannin in	One foot from root	Middle of trunk	Thin end of trunk
Beech bark with bast:			
Highest percentage	4.78	6.01	7.24
Lowest percentage	2.64	2.72	3.99
Mean for the year	3.78	4.64	5.58
Larch bark:			
Highest percentage	3.89	7.27	9.54
Lowest percentage	1.26	3.34	5.82
Mean for the year	2.54	4.40	7.40
Larch bast:			
Highest percentage	12.63	15.70	16.36
Lowest percentage	8.40	9.33	10.56
Mean for the year	10.15	12.30	15.53

In every case the proportion of tannin increases from below upwards, and is greatest at the summit of the tree; this was found true at all times of the year. The bast of larch is seen to be far richer in tannin than the bark. With beech bark the maximum of tannin occurred in winter, and the minimum in July. With larch bark and bast the minimum was found about December; the maximum, in the case of bast, occurred in April or May; with the bark the maximum was irregular.

The percentage of tannin in the dry substance of various parts of the oak is, according to T. Hartig, as follows:

Heart wood—tree 160 years old; winter	12-14 per cent.
Old Bark	10-14 "
" " the outer layer	6 "
" " the middle layer	12 "
" " the bast layer	14-18 "
Young bark (Spiegelrinde)	9-18 "
Brush wood; November to end of February	11-15½ "
" " May to June	4-7 "
Young shoots and buds; beginning of May	24 "

According to Handtke the last year's shoots of oak yielded on April 23, 7.83 per cent. of tannin; this gradually increased to 14.85 per cent. on July 9, after which the percentage diminished. In Valonia, the acorn cups of *Quercus Egilops*, the percentage of tannin is about 19-27. In Levant nut-galls, the excrescences on the young shoots of *Q. infectoria*, the tannin is about 50-60 per cent. For further information, see articles—GALL-NUTS, QUERCUS, TANNIN, in this Dictionary.

The distribution of resin in trees has been little investigated. Ulbricht has determined the resin present in spruce fir-wood at different times of the year; as resin he includes all organic matter soluble in alcohol, but not in water. 1,000 of dry wood contained:

	Sap wood	Heart wood	Entire wood
Winter	19.66	22.99	22.13
Spring	17.81	20.41	19.11
Summer	19.87	22.35	21.09
Autumn	20.24	21.58	21.37

The heart wood is thus richer in resin than the sap wood.* The maximum percentage of resin is apparently in winter, and the minimum in spring; the details are irregular.

Few determinations have been made of the uitrogenous ingredients of wood. The most complete series of analyses is by Schroeder and Karsten* (*Tharander*

* These determinations were made by combustion with soda-lime, collecting the ammonia in hydrochloric acid, then evaporating to dryness the acid liquid, and determining the chloride of ammonium in the residue with a standard solution of silver.

forstliches Jahrbuch, 1874, 70, 179). Schroeder determined nitrogen in every 10 year-rings of an 80-years old beech tree. In the youngest 10 rings the nitrogen amounted to 0.22 per cent. of the dry wood; the older wood was rather poorer in nitrogen, but there was no regular gradation from the new to the old wood. The mean per cent. of nitrogen in the sap wood was 0.17, and in the heart wood 0.16. The proportion of nitrogen was much greater in the wood of the branches, increasing as they diminished in size; it was also considerable in the bark. Schroeder found the following percentages of nitrogen in dry beech wood and bark:

Trunk wood, without bark	0.16
Stout boughs	0.26
Boughs 7-2.5 cm. diam. without bark	0.32
" 2.5-1.0 "	0.50
" 1-0.5 "	0.63
Bark from trunk	0.56

In the case of spruce fir, Karsten determined nitrogen in trees felled every month during a year; in the same specimens Ulbricht determined the proportion of nitrogenous matter soluble in water. 100 of dry trunk wood yielded, on an average of two trees, the following percentages of nitrogen:

	Total nitrogen			Soluble nitrogen		
	Sap wood	Heart wood	Entire wood	Sap wood	Heart wood	Entire wood
Winter	0.150	0.184	0.171	0.0160	0.0080	0.0130
Spring	0.169	0.141	0.154	0.0052	0.0023	0.0036
Summer	0.261	0.265	0.259	0.0123	0.0062	0.0090
Autumn	0.197	0.167	0.183	0.0137	0.0046	0.0090
Mean for the year	0.194	0.180	0.192	0.0116	0.0053	0.0087

The sap wood contains scarcely more total nitrogen than the heart wood, but a more considerable proportion of this nitrogen exists as soluble compounds. The soluble nitrogen is at its maximum in winter, and at its minimum in spring time when active growth has commenced. The total nitrogen is at its maximum in summer.

O. Lehmann (*Chem. Ackermann*, 1869, 118) found in fresh sawdust from spruce fir wood, 0.67 per cent. of nitrogen, and in sawdust from Scotch pine, 0.53 per cent. These results are much higher than those of Schroeder and Karsten.

Ash constituents occur in very different proportions in the various parts of a tree. The circulating ash constituents, which act as plant food, are concentrated in the actively growing tissues; the incrusting ash constituents, on the other hand, accumulate with advancing age, and especially in the surface tissues of the tree; the variations in the percentage of ash are thus due to very different causes. Wood contains much less ash than bark, and this again less than the leaves. Young wood generally contains more ash than old wood. It follows that the percentage of ash in the trunk rises from below upwards, and that branches contain more ash than the parent stem, the smaller branches being again richer in ash than the larger ones. Of the bark, the inner bast layer is much the richest in ash constituents; young bark will thus yield more ash than the thick bark found on older parts of the tree. The ash of the bark is always greater than that of the wood it covers.

The following percentages of crude ash were found by Stöckhardt and Handtke (*Jahresb. Agri. Chem.* 1864, 81) in dry wood and bark taken at various heights of the trunk:

Crude ash in 100 of			Upper	Crude ash in 100 of			Upper
Beech wood	0.43	0.45	0.57	Beech bark	3.90	3.30	3.00
Larch wood	0.27	0.30	0.37	Larch bark	1.25	1.75	2.15
Spruce fir wood,	0.32	0.33	0.41	Spruce fir bark,	3.66	3.01	2.60
quickly grown				quickly grown			
Spruce fir wood,	0.35	0.39	0.47	Spruce fir bark,	4.77	4.29	4.53
slowly grown				slowly grown			

The results obtained by R. Weber (*Jahresb. Agri. Chem.* 1873-4, i. 245) in his

analysis of a larch, 40-50 years old, strikingly illustrate the relation in respect to ash of the old and new layers of growth. 100 of dry substance contained:

	Crude ash
Heart wood	0.14
Sap wood	0.30
Last year's ring	0.48
Cambium with bast bundles	5.17

The relative distribution of ash-constituents in trunk, branches, and leaves, is well shown by the following results obtained by J. Schroeder from an examination of a birch tree felled in August, and of a spruce fir, 90 to 100 years old, felled in May. 100 of dry substance contained:

Birch	Pure ash	Spruce fir	Pure ash
Wood from trunk	0.21	Wood from trunk, breast high	0.17
Wood from boughs	0.64	Wood from trunk, upper part	0.26
Bark from trunk	0.62	Wood from boughs, over 1 cm. diam.	0.32
Bark from boughs	3.44	Bark from trunk, breast high	1.38
Leaves	4.53	Bark from trunk, upper part	1.84
		Bark from boughs, over 1 cm. diam.	2.82
		Leaves	3.59

The percentage of ash in all the growing parts of a tree exhibits considerable variation at different periods of the year. Stöckhardt determined the ash at various heights in the trunk wood and bark of beech and larch every month during a year. The following is a summary of his results; the figures represent the proportion of crude ash in 100 dry substance:

	Lower	Middle	Upper		Lower	Middle	Upper
Beech bark:				Larch bark:			
Winter	3.40	2.60	2.31	Winter	1.04	1.75	2.33
Spring	5.86	4.39	4.40	Spring	1.40	2.10	2.18
Summer	5.20	3.04	2.68	Summer	1.27	1.70	2.11
Autumn	3.30	3.03	2.39	Autumn	1.06	1.34	1.93
Beech wood:				Larch wood:			
Winter	0.11	0.46	0.67	Winter	0.25	0.32	0.41
Spring	0.45	0.43	0.47	Spring	0.27	0.33	0.38
Summer	0.44	0.46	0.55	Summer	0.25	0.26	0.33
Autumn	0.43	0.46	0.62	Autumn	0.29	0.30	0.41

We shall better understand these results if we first compare the results obtained by Schroeder with spruce fir:

Pure ash in 100 parts of dry fir wood	Sap wood	Heart wood	Entire wood
Winter	0.2427	0.2270	0.2304
Spring	0.2364	0.2319	0.2335
Summer	0.2288	0.2317	0.2281
Autumn	0.2488	0.2404	0.2449
Mean for the year	0.2392	0.2328	0.2342

The ash is at its maximum in sap wood in autumn and winter, but in the bark the ash is at its minimum at this period; in the old wood it also reaches its minimum in winter. In spring the ash in the sap wood falls, and at the same time rises considerably in the bark, in the innermost layer of which active growth has commenced; the ash also rises to a less extent in the old wood. By summer, both the sap wood and bark have reached their minimum, the circulating ash-constituents having been transferred to the leaves. When the leaves wither, a portion of the ash-constituents is again stored up in the sap wood for use in the ensuing season. In Stöckhardt's experiments the upper and younger part of the trunk exhibits the character of sap wood, and the lower and older portion the character of heart wood.

The proportion of ash-constituents in any tree is dependent to a considerable extent on the character of the soil and climate. A tree growing in the rich soil and mild climate of a valley, will contain in its tissues a far larger proportion of cinereal matter than the same description of tree growing in an elevated mountain region. The influence of the soil upon the character of the ash will be illustrated further on.

We turn now to the composition of wood and bark ash: a selection of analyses will be found on the next page. Nos. 1-21, and 33-34, are taken from E. Wolff's *Aschen Analysen*; Nos. 22-32 are from the *Tharander forstliches Jahrbuch*, 1874, 58, 274. Analyses 3-5, 7-15, 16-21, 22-23, 24-32, and 33-34, are respectively comparable among themselves, being made either on different parts of a single tree, or on trees taken from the same plantation. The birch tree was analysed by Schroeder; it was felled towards the end of August. The analyses of spruce fir (22-32) are also by Schroeder. The first series (22-23) are from a tree felled in February. The second tree was analysed in all its parts; it was 90-100 years old, and was felled in May. The 'pure ash' is the ash remaining after deduction of carbonic acid, sand, and charcoal. The carbonic acid given in Nos. 7-15, and 24-32, includes sand and charcoal. Alumina is an ingredient of several of the ashes in the table, though not mentioned there; it is particularly large in the ashes of the spruce fir analysed by Wittstein. The three wood ashes (16-18) gave respectively 1.09, 0.90, and 0.33 per cent. alumina, and the three bark ashes (19-21) 12.20, 5.67, and 4.46 per cent.

The percentage composition of an ash merely teaches us the proportion in which the various constituents stand to each other, and throws but little light on the proportion or distribution of ash-constituents in the plant. Some local circumstance, as the presence of much manganese or soluble silica in the soil, will suffice to alter completely the percentage of phosphoric acid or potash in the ash, while the proportion of these important elements in the dry matter of the plant may remain quite unaffected. We must, therefore, regard not only the percentage composition of the ash, but also the proportion of ash-constituents in the dry substance of the wood and bark.

Good illustrations of the difference in the ash contents of old and new wood and bark are afforded by R. Weber's analyses of the various layers in the trunk of a larch; by Schroeder's analyses of sap and heart wood from a spruce fir; and by his analyses of the outer and inner layers of bark from the same tree. The figures given below for spruce fir wood are the mean of four analyses of trees felled in each quarter of the year. 10,000 parts of dry substance contained as follows:

	K ² O	Na ² O	CaO	MgO	Fe ² O ³	Mn ² O ³	P ² O ⁵	SiO ²	SO ²
Larch:									
Heart wood . . .	1.23	0.26	4.83	1.32	0.47	—	0.36	0.24	1.07
Sap wood . . .	6.45	0.50	8.95	1.82	0.95	—	2.76	0.25	1.13
Cambium and bast	108.60	19.20	228.10	17.90	1.40	—	32.80	3.90	1.00
Spruce fir:									
Heart wood . . .	3.43	0.40	6.69	2.26	0.12	5.11	0.08	0.49	—
Sap wood . . .	4.58	0.27	6.58	2.02	0.22	5.23	0.86	0.88	—
Outer bark . . .	4.50	0.70	63.30	4.10	5.50	9.50	2.30	8.80	46.1
Inner bark . . .	32.20	4.10	100.80	14.90	1.00	33.30	3.50	1.40	6.1

It is evident that as new tissue matures, the circulating ash-constituents are gradually withdrawn, and made to serve anew in fresh cell formation. The same ash-constituents thus serve over and over again in the production of organised matter. The most striking difference in the ash contents of heart and sap wood lies in the proportion of phosphoric acid, which is nine or ten times greater in the young wood than in the old; the sap wood also contains a larger proportion of potash. When we turn to the cambium—the layer of tissue in which growth is actively in progress—we find all the ash-constituents in very large proportion, the phosphoric acid and potash are especially about one hundred times greater than in the heart wood. The younger layers of bark of the spruce fir are also much richer in ash-constituents than the old exterior layers; these latter contain, however, more silica, iron, and sulphuric acid. Manganese appears to form part of the circulating ash-constituents, and is most abundant in young tissue.

Analyses of the Ash of Wood and Bark.

No.		Ash in 100 of dry substance		Composition of 100 parts of pure ash										Carbonic acid in 100 of crude ash	
		Crude ash	Pure ash	Potash	Soda	Lime	Magnesia	Ferric oxide	Manganese oxide	Phosphoric acid	Sulphuric acid	Silica	Chlorine		
Willow:															
1	Young stems cut in September	—	2.88	34.09	—	41.13	5.96	0.53	0.15	12.99	2.65	0.12	0.47	—	33.86
Beech:															
2	Trunk wood	0.74	0.49	18.42	1.26	62.14	4.55	0.75	2.37	4.59	0.55	5.09	0.19	—	19.60
3	* Large logs, with bark.	—	—	16.38	3.85	49.48	12.54	0.64	1.15	7.53	0.57	7.78	0.08	—	17.41
4	* Small logs, "	—	—	15.15	2.09	45.84	16.23	1.53	0.09	11.64	0.67	6.89	0.06	—	16.31
5	* Faggot wood, "	—	—	14.11	2.18	48.01	10.82	0.71	0.71	12.30	1.18	9.85	0.13	—	—
6	Bark of old tree	—	4.45	14.72	0.36	57.90	0.24	1.82	5.97	0.36	1.33	17.97	—	—	—
Birch:															
7	Trunk wood, centre	0.40	0.30	10.11	6.78	49.82	11.98	1.26	—	16.59	2.70	0.77	—	—	24.71
8	" outer layers	0.22	0.16	20.78	10.82	41.11	11.10	1.43	—	11.04	2.52	1.21	—	—	28.63
9	" entire	0.25	0.21	15.12	8.68	45.79	11.69	1.34	—	14.03	2.59	0.85	—	—	26.75
10	Wood from branches	0.84	0.64	26.95	1.29	32.72	11.72	0.73	—	17.98	4.11	0.41	3.96	—	24.42
11	Bark from trunk.	1.16	0.78	10.08	—	74.30	8.39	0.24	—	7.74	1.46	0.73	0.05	—	37.11
12	White rind from trunk	0.47	0.38	8.43	3.09	48.58	13.98	5.25	—	12.77	2.75	4.11	1.03	—	18.88
13	Entire bark from trunk	0.93	0.62	9.84	0.64	69.09	7.11	1.27	—	8.69	1.70	1.42	0.24	—	33.04
14	" from branches	5.38	3.46	13.91	—	69.51	6.00	1.09	—	7.39	1.19	0.50	0.34	—	36.04
15	Leaves	6.39	4.53	23.33	2.65	39.29	15.35	1.51	—	13.29	1.71	2.26	0.59	—	29.14

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Spruce fir														
16	Trunk wood, tree 220 years' old.	0.45	0.38	8.43	5.30	29.41	6.80	5.88	—	4.69	2.42	36.18	0.43	16.26
17	" " 172 "	0.58	0.46	15.31	3.94	47.84	4.65	2.40	0.07	3.41	2.38	18.03	0.71	20.12
18	" " 135 "	0.43	0.33	3.60	4.28	46.49	5.32	10.07	0.21	3.51	1.74	15.41	0.61	22.98
19	Bark, tree 220 years old.	1.13	0.94	2.14	0.98	27.44	1.90	7.80	—	6.43	1.72	39.20	0.18	16.93
20	" " 172 "	1.98	1.57	2.67	1.53	45.91	2.03	2.67	0.65	8.54	0.54	30.45	0.14	20.71
21	" " 135 "	2.92	2.02	1.06	0.39	60.38	0.92	0.49	—	10.37	—	21.23	0.07	30.91
22	Heart wood	—	0.17	18.55	1.84	34.79	13.55	0.10	26.27	0.46	3.38	0.94	0.02	—
23	Sap wood	—	0.18	22.61	2.10	33.38	9.88	1.66	21.49	3.82	4.40	0.81	0.05	—
24	Wood, from trunk	0.21	0.17	20.42	0.47	39.82	9.25	0.79	22.47	2.49	1.10	2.98	0.11	20.35
25	" upper part of trunk.	0.30	0.26	19.69	1.07	34.43	9.84	1.22	26.02	4.65	1.18	1.88	0.12	12.40
26	" boughs over 1 cm. diam.	0.39	0.32	19.64	1.45	38.73	11.39	0.96	22.86	1.98	1.38	1.61	—	18.06
27	Bark, from trunk	1.75	1.38	8.48	2.11	51.65	5.27	4.43	12.98	4.32	2.19	8.34	0.23	21.36
28	" upper part of trunk	2.12	1.84	20.82	0.92	36.56	8.47	2.25	13.42	6.33	1.74	8.28	0.71	13.10
29	" boughs, over 1 cm. diam.	3.45	2.82	12.12	4.49	41.65	6.75	2.59	12.07	4.68	1.13	14.01	0.51	18.41
30	Whole boughs, over 1 cm. diam.	1.18	0.97	13.96	3.75	40.93	7.89	2.20	14.71	4.02	1.19	10.97	0.38	—
31	" under 1 cm. diam.	2.01	1.87	18.07	1.88	22.15	1.98	4.77	9.04	9.20	3.13	24.43	0.35	6.99
32	Leaves	3.82	3.59	11.31	2.34	12.58	5.37	1.17	8.16	9.93	4.21	46.01	0.95	6.00
Scotch pine:														
33	Large logs, with bark.	—	—	15.11	0.54	62.10	10.42	0.76	0.48	6.24	1.32	3.02	0.04	19.06
34	Small logs	—	—	17.05	2.84	57.62	10.06	0.89	0.80	6.88	1.93	3.31	0.11	17.56

* Large logs (Scheitholz) are apparently those parts of the trunk and larger branches which must be split to form billets. Small logs (Prügelholz) require no splitting to form billets. Pallet wood (Bretscholz) consists of the smaller branches and twigs. German writers classify the produce of a forest under these three heads.

Stöckhardt has determined the phosphoric acid in the wood and bark of a beech tree during a whole year, and at various heights of the trunk; the average quantities found were as follows:

Phosphoric acid in 100 parts of ash.

	Lower	Middle	Upper
Beech wood .	5.74	7.07	13.43
Beech bark .	3.80	4.68	5.58

Phosphoric acid in 10,000 of dry substance.

	Lower	Middle	Upper
Beech wood .	2.51	3.18	7.49
Beech bark .	14.82	15.25	

Phosphoric acid thus increased in the trunk from below upwards. Phosphoric acid is always found concentrated in those parts in which growth is proceeding; it is found in larger proportion in the branches than in the trunk, and increases in the branches as they diminish in diameter. This variation in the proportion of phosphoric acid is generally sufficient to affect distinctly the percentage composition of the ash.

Potash is also abundant in young growth, but this is not invariably seen by the percentage composition of the ash, though always evident when the composition of the dry substance is regarded. The percentage of potash is affected a good deal by the composition of the soil; on a calcareous soil more lime and less potash will be found in the ash.

Since young stems, branches, and twigs, are so especially rich in ash-constituents, and particularly in those most important ones, phosphoric acid and potash, it follows that it will be far more exhausting to the soil to grow pole or faggot wood than to produce full-sized timber. Ebermayer (*Gesammte Lehre der Waldstreu*, 112) calculates that 1 cubic meter of large logs (*Scheitholz*), small logs (*Prügelholz*), and faggot wood (*Reisigholz*), will contain respectively in grams the following amounts of ash-constituents:

	Total pure ash	K ² O	CaO	MgO	Fe ² O ³	P ² O ⁵	SO ²	SiO ²	Cl
Beech, large logs . . .	5102	836	2524	640	33	385	29	397	4
" small logs . . .	8455	1282	3878	1373	27	980	57	566	6
" faggot wood . . .	11840	1671	5684	1283	84	1458	140	1165	14
Spruce fir, large logs . .	1620	230	750	117	44	56	27	95	3
" " small logs . . .	2790	569	998	251	51	158	42	170	14
" " faggot wood . . .	10973	1432	2146	672	222	956	379	3950	80
Scotch pine, large logs . .	1100	166	682	114	8	69	15	43	1
" " small logs . . .	1411	217	815	142	13	97	27	47	2
" " faggot wood . . .	4675	793	2150	554	53	626	91	287	3

These figures are deduced from a limited series of analyses, and must not be taken too absolutely as expressing the actual requirements of different trees; they plainly show, however, the far greater exhaustion of the soil which attends the frequent cutting of young wood, than by the cultivation of full-sized timber. Nature is especially careful to preserve undiminished all the more valuable ash-constituents. Schroeder has shown that when a bough naturally withers upon the trunk, the greater part of the phosphoric acid and potash are resorbed into the parent stem before the bough falls; the lime and silica are not thus cared for, but remain in the withered branch.

Bark always contains, in relation to its dry substance, a greater quantity of all the ash-constituents than the wood it covers, the proportion of the ash-constituents to each other is, however, different from that in wood. In bark ash there is generally a smaller percentage of potash and magnesia, and a larger proportion of lime, silica, and perhaps alumina, than in wood ash. The outermost layer of bark is especially rich in silica. Beech bark possesses a remarkably perfect skin of silica, and may, according to Ebermayer, be burnt without destroying the forms of the cells. Many trees, as maple and elm, have a similar but less perfect coating of silica. This siliceous skin

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is doubtless important as protecting the stem from the infiltration of water, and from the attacks of fungi and insects. The ash analyses of spruce fir given in the table, page 807, show that the percentage of silica in the ash increases with increasing age, while the percentage of lime diminishes. Fir-timber grown on a siliceous soil is reckoned more durable than that grown on a calcareous soil.

Manganese is generally found in the ash of trees if present in the soil upon which they have grown; the quantity is extremely variable, but is sometimes very large. Berthier found in the ash of oak bark 11.38 per cent. MnO ; Böttiger, in the ash of larch wood 13.5 per cent., and in wood from a Scotch pine 18.2 per cent.; while Schroeder has found as much as 32.77 per cent. in the ash of spruce fir wood. The proportion of manganese is generally much smaller. Leclerc's determinations in various woods will be found in *Jahresb. Agri. Chem.* 1870-2, ii. 21. Manganese exists in trees in a soluble form, probably as salts of manganous oxide.

Carbonic acid is a large ingredient in the ash of wood; it represents, in the absence of much silica, the organic acids originally united with the bases of the ash. The proportion of bases combined with organic acids is apparently greater in old wood than in young.

We will conclude these remarks on the distribution of the ash-constituents in a tree, by giving the results obtained in Schroeder's admirable investigation of an entire spruce fir felled in May. 10,000 parts of dry substance contained as follows:

	K ² O	Na ² O	CaO	MgO	Fe ² O ³	Mn ² O ³	P ² O ⁵	SO ²	SiO ²
Wood:									
Trunk wood . . .	3.45	0.08	6.73	1.58	0.13	3.80	0.42	0.19	0.50
Ditto, upper portion .	5.12	0.51	8.95	2.56	0.32	6.50	1.21	0.31	0.49
Wood from boughs over 1 cm. diam. }	6.28	0.47	12.30	3.64	0.31	7.32	0.63	0.44	0.52
Bark:									
Trunk bark . . .	11.67	2.90	71.07	7.25	6.10	17.86	5.94	3.01	11.48
Ditto, upper portion .	38.35	1.70	37.34	15.60	4.14	24.72	11.66	3.21	16.17
Bark from boughs over 1 cm. diam. }	34.12	12.63	117.23	19.01	7.28	33.98	13.18	3.18	30.44
Boughs with bark over 1 cm. diam. }	13.40	3.61	39.58	7.62	2.12	14.23	3.88	1.15	10.65
Boughs with bark under 1 cm. diam. }	33.79	3.52	41.42	13.05	8.93	16.91	17.21	5.85	45.67
Leaves . . .	40.61	1.12	45.15	19.29	4.20	29.30	35.64	15.13	165.26

The leaf contains in relation to its dry substance the largest proportion of potash, magnesia, phosphoric and sulphuric acids, chlorine, and silica. The bark of the small boughs is richest in soda, lime, ferric oxide, and manganese. The trunk wood is of the whole tree the part poorest in ash-constituents.

Schroeder has made the results still more striking by reckoning the total amount of each ash-constituent as 100, and showing the distribution of these 100 parts throughout the tree; the following are the figures:

	Dry sub- stance	Potash ash	MgO						
Trunk wood . . .	76.0	23.0	34.0	28.2	32.1	38.8	9.7	10.1	3.2
" bark . . .	10.6	26.3	18.1	41.6	21.6	47.9	25.4	19.0	21.8
Boughs with bark	8.3	18.7	21.7	18.3	20.7	28.0	16.5	20.0	15.7
Leaves . . .	5.1		26.2	12.5	25.6	16.1	19.3	51.3	52.4
Entire tree	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

The dry matter of the leaf is only 5.1 per cent. of the whole tree, yet the leaf contains nearly one-third of the entire ash, more than half of the whole phosphoric and sulphuric acids, and nearly three-quarters of the silica. Lime and iron are seen to be chiefly concentrated in the bark. The trunk wood contains a considerable

* All the figures relating to Schroeder's investigation of spruce fir are taken from the *Tharander forstliches Jahrbuch*, 1874; these figures differ in many respects from those given in the *Chemische Actermannann*, 1873. The publication of later date is adopted as presumably more correct.

fraction of the ash-constituents only in the cases of manganese oxide, potash, magnesia, and lime. The difference in occurrence of iron and manganese is very striking, the first being found chiefly in the bark, the second in the wood.

The alteration in the composition of the ash at various seasons of the year has been studied by Schroeder in the case of spruce fir wood, and by Stöckhardt, as far as phosphoric acid is concerned, in the case of beech wood and bark. Neither of these investigations has led to particularly striking results. Nearly all the ash-constituents of wood are at a minimum in summer time, having been more or less transferred to the growing shoots and leaves. Manganese is apparently an exception to this rule, as Schroeder found it most abundant in August. Staffel's analyses of the ash of one-year shoots of horse-chestnut in May and September will be found in this Dictionary, iii. 174.

The influence of the character of the soil upon the composition of the ash of trees is well illustrated by the investigations of Fliche and Grandeau (*Ann. Chim. Phys.* [4], xxix. 383; [5], ii. 354). They observed that the sweet chestnut, and certain pines, did not flourish in a part of the forest of Champéty, where the soil was calcareous, though perfectly healthy where the soil was of a siliceous character. The following are ash analyses of small branches and leaves of chestnut, and *Pinus Pinaster*, grown upon the two soils in question:

	<i>Pinus Pinaster</i> , small branches with leaves		Chestnut, small branches		Chestnut leaves	
	Siliceous soil	Calcareous soil	Siliceous soil	Calcareous soil	Siliceous soil	Calcareous soil
Ash, per cent.	1.32	1.54	4.74	5.71	4.80	7.80
Potash	16.04	4.95	11.65	2.69	21.67	5.76
Soda	1.91	2.52	—	0.28	3.86	0.66
Lime	40.20	56.14	73.26	87.30	45.37	74.55
Magnesia	20.09	18.80	3.99	2.07	6.63	3.70
Ferric oxide	3.83	2.07	2.04	1.27	1.07	0.83
Phosphoric acid	9.00	9.14	4.53	4.27	12.32	12.50
Sulphuric acid	—	—	1.43	0.64	2.97	—
Silica	9.18	6.42	3.08	1.36	5.79	1.46
Chlorine	—	—	—	0.08	0.30	0.52

It is seen at once that the ash is in all cases greater in quantity on the calcareous soil; but contains less silica, far less potash, and more lime, than the ash of the same tree growing upon the siliceous soil. Further illustration of the effect of soil and climate upon the character of the ash will be found in R. Weber's researches (*Jahresh. Agri. Chem.* 1873-4, i. 245) on the composition of larch wood and leaf at different altitudes. The subject will also be again referred to under the head of 'The Leaf.'

Schroeder has made an investigation upon the solubility of the ash-constituents in spruce fir (*Tharander forstl. Jahrbuch*, 1874, 52). Spruce fir sawdust yielded to cold distilled water about 23 per cent. of the total ash which it contained, the part dissolved consisted chiefly (72.96 per cent.) of potash; the sawdust lost in this way 75 per cent. of the potash previously present. A log placed in running water for two years, showed a similar loss in potash, and also a striking loss in manganese. The sap wood of the log lost 32 per cent. of its entire ash, the heart wood 10 per cent. In the sap wood, 84 per cent. of the potash had been removed, and 72 per cent. of the manganese. The heart wood lost 71 per cent. of its potash, and 51 per cent. of its manganese. There was also a loss of sulphuric acid, and a gain in lime and iron. Schroeder carried the investigation further by treating spruce fir sawdust with a solution containing the chlorides of potassium and calcium. To this solution the wood yielded up all its potash, more than two-thirds its magnesia, and nearly half its manganese, absorbing at the same time from the solution a very considerable quantity of lime. It is evident from these experiments that the potash of wood exists in the form of soluble, probably organic, salts, and that the woody tissue has for these a very small retentive power. It is quite otherwise with respect to lime; this exists in the wood as insoluble salts, and wood exhibits for lime a considerable absorptive and retentive power. It is probable that the organic acids of wood form with lime insoluble compounds, and that for this reason lime is able to displace the other bases, as shown in

Schroeder's last quoted experiment. The effect of floating timber down a river is clearly to remove a large proportion of potash from the wood.

2. THE SAP.

The chemistry of the sap has been investigated only in the case of birch, maple and hornbeam, trees which bleed if cut in early spring. J. Schroeder has experimented with birch (*Jahresb. Agr. Chem.* 1865, 157), and with birch and maple (*ibid.* 1870-2, ii. 149). A. Beyer has investigated the sap of birch and hornbeam (*ibid.* 1865, 167; 1867, 109).

Schroeder states that in birch the transformation of starch into sugar begins in the parenchyma of the bark, the upper branches being the part of the tree first affected, and the trunk wood and root the parts where starch is longest held. The change into sugar is apparently commenced by the influence of the sun's rays, and precedes the rising of the sap. On Feb. 3, no sugar was found in borings from the trunk and root of a birch. On March 12, the borings yielded sugar. On March 17, the borings were found moist and sticky, and seven days later the sap began to flow. Sap can first be obtained by a boring in the root; it then rises gradually in the trunk at the rate of about 1 meter in two days. When the highest point has been reached at which bleeding will take place, the flow of sap begins to diminish, gradually ceasing from above downwards, and continuing a short time in the root after it has ceased in the trunk. With birch, bleeding begins about a week earlier, and continues about a week later than with maple. The whole bleeding period with birch is about six or seven weeks.

The principal ingredient in spring sap is sugar. In birch sap the sugar is laevorotatory, uncrystallisable, and easily soluble in hot 95 per cent. alcohol. In the sap of hornbeam, osimililar sugar is present. In maple sap, on the other hand, the sugar is wholly cane-sugar. The percentage of sugar in birch sap was found by Schroeder to vary between 0.34 and 1.92, and that in maple sap from 1.15 to 3.71. Beyer found in hornbeam sap 0.46 per cent. of sugar.

The percentage of sugar in the sap flowing from any part of the trunk reaches its maximum very soon after bleeding commences, and then diminishes till bleeding ceases. Thus sap from a boring at the foot of a birch tree commenced running on April 5, it then contained 1.25 per cent. of sugar. On April 9 the sugar had reached 1.40 per cent. From this point the percentage of sugar diminished to 0.69, which it reached on May 22, when bleeding stopped. The quantity of sugar in the sap is increased in the earlier part of the season by a rise in temperature. The percentage of sugar falls rapidly as soon as leaf buds begin to develop, and the stage of development reached by the leaf forms an excellent indication of the condition of the sap.

The part of the tree yielding the sap richest in sugar is differently situated in birch and maple. With birch, the richest sap is obtained from some point in the trunk between the root and the principal branches; above this point the percentage of sugar rapidly diminishes. Thus on April 14, sap from the foot of a birch trunk contained 1.39 per cent. sugar; at 3 meters height 1.60 per cent.; and at 7 meters height 0.74 per cent. As the season advances, the point of maximum sugar falls lower and lower in the trunk, but never enters the root. In the root the percentage of sugar decreases with the distance from the trunk. With maple, on the other hand, the richest sap is obtained from the highest borings, and the sap of the root is richer than that from the lower part of the trunk. The difference between the two trees is to be attributed partly to the greater store of reserve starch contained in maple, and especially in the thinner branches forming the extremities, but is also due to the fact that leaf buds are not developed in maple till bleeding ceases. There is thus in maple both a greater production, and a smaller consumption of sugar during the bleeding period, and hence the sap gains in richness as it ascends, and, unlike the sap of birch, maintains the same percentage of sugar till nearly the end of the bleeding period.

No detailed investigation seems to have been made upon the American maple, *A. saccharinum*. The sap is variously stated to contain 2 and 6 per cent. of sugar. The Canadian trees yield an average of 4 lbs. of sugar each.

Of the presence of carbo-hydrates other than sugar no definite evidence exists. The sap of the three trees investigated was always acid with malic acid. A litre of birch sap, from near the foot of the trunk, contained on April 11, 0.3324 gram of malic acid; the quantity gradually rose to 0.6071 gram on April 27, and then fell to 0.3459 gram on May 13.*

The amount of albumin (determined by boiling the sap) rises for a short time

* The dates and figures referring to birch are from the *Landes. Versuchs-Stationen*, liv. 121, 122. The *Jahresbericht* gives the same figures but with different dates.

after bleeding commences, and then falls more rapidly than the sugar. Schroeder found in 1 litre of birch and maple sap, taken near the foot of the trunk, the following quantities in grams:

Birch sap			Albumin	Sugar	Maple sap			Albumin	Sugar
April 10 . . .			0.0200	14.0	April 30 . . .			0.0186	28.9
April 16 . . .			0.0330	12.0	May 3 . . .			0.0238	24.9
May 1 . . .			0.0176	10.3	May 7 . . .			0.0152	23.2
May 19 * . . .			0.0069	9.4	May 16 . . .			0.0079	19.2

The quantity of nitrogen in sap far exceeds that of the coagulable albumin. Beyer found in 1 litre of birch sap 0.052 gram of albumin, but 0.238 gram of total nitrogen. A litre of hornbeam sap yielded 0.224 gram of nitrogen. Calculated on the dry matter of the sap, the total nitrogen was in the case of birch 1.9, and with hornbeam 3.4 per cent. Ammonium salts, and a crystallisable body which appears to be asparagin, are among the nitrogenous substances present.

The total ash-constituents contained in the sap increases rapidly in the case of birch after bleeding has commenced, and falls but little towards the end of the bleeding period. Thus a litre of birch sap, taken near the ground, contained on April 11, 0.50 gram of ash; on May 2, it had reached its maximum of 1.08 gram; and on May 18, at the end of the bleeding period, it had fallen to 0.97 gram. The proportion of ash is greatest in the sap from the lower part of the trunk, diminishing both in the higher parts of the tree and in the root. With maple, on the other hand, the percentage of ash does not apparently diminish at higher parts of the trunk, and it is greater in the root than in the lower part of the trunk. The distribution of ash in these trees is thus similar to the distribution of sugar, and is doubtless in part due to the different period of leaf development already noticed. It is evident that sap must become more concentrated in the higher parts of a tree, by the evaporation of a portion of its water; if, however, the soluble matters are at the same time removed to form tissue, the sap may become weaker.

The nature of the ash yielded by birch sap, and its variation at different heights and dates, will be seen from the following results obtained by Schroeder. The lower sap was taken at 0.28 meter from the ground, the upper sap at 7.33 meters. The root sap was from a point 2.9 meters from the trunk; the trunk sap, taken the previous day for comparison, was obtained 0.2 meter from the ground. 10 litres of sap contained in grams:

Birch sap	April 18		April 22-23		April 30		May 9	May 10
	Lower sap	Upper sap	Lower sap	Upper sap	Lower sap	Upper sap	Trunk sap	Root sap
Total crude ash . . .	5.20	2.90	8.20	4.20	11.40	5.40	8.70	6.80
Potash	0.848	0.873	6.893	1.009	1.000	1.298	1.404	1.502
Soda	0.109	0.078	0.107	0.078	0.235	0.115	0.279	0.272
Lime	1.627	0.456	3.180	1.166	4.530	1.423	2.540	1.586
Magnesia	0.403	0.204	0.705	0.360	0.476	0.434	0.973	0.647
Ferric oxide	0.011	0.006	0.031	0.011	0.046	0.020	0.085	0.067
Phosphoric acid	0.262	0.222	0.350	0.265	0.862	0.290	0.291	0.335
Sulphuric acid	0.104	0.061	—	—	—	—	—	—

The first six analyses refer to the period in which the total ash increases in weight. The increase in the lower sap is chiefly an increase in lime and phosphoric acid; the increase in the upper sap is principally lime and potash. The sap in passing from the lower to the upper part of the trunk loses a portion of each ash-constituent, except potash, the loss being greatest in the case of lime and phosphoric acid. The missing ash-constituents have doubtless been appropriated to the construction of new tissue; their diminution is most marked at the latest date, when leaf development had probably commenced. The increase of potash in the upper sap is certainly remarkable; possibly the potash stored up in autumn out of the withering leaves is liberated again on the solution of the starch. The root sap, 2.9 meters from the trunk, contains

* The dates and figures referring to birch are from the *Landw. Versuchs-Stationen*, xiv. 131, 132. The *Jahresbericht* gives the same figures, but with different dates.

more potash and phosphoric acid, and less lime and magnesia, than that from the trunk of the tree.

Schroeder's ash analyses of maple sap are given in the following table. The root sap was taken 1 meter from the trunk; the trunk sap for comparison was from a height of 0.25 meter. 10 litres of sap contained in grams:

Maple sap	April 28	May 5	May 18	May 5			May 5	
	Height 0.3 m.	Height 0.3 m.	Height 0.3 m.	Height 0.3 m.	Height 3.3 m.	Height 5.8 m.	Trunk sap	Root sap
Total crude ash . . .	12.2	10.9	9.3	10.9	10.2	13.2	6.3	9.5
Potash	2.708	3.529	3.009	3.529	3.321	1.345	1.661	1.857
Soda	0.096	0.040	0.073	0.040	0.321	0.182	0.056	0.138
Lime	2.404	2.262	1.462	2.262	2.142	2.655	1.798	0.644
Magnesia	0.584	0.660	0.524	0.660	0.673	0.921	0.304	0.281
Ferric oxide	0.050	0.012	0.091	0.012	0.112	0.067	0.019	0.025
Phosphoric acid	0.968	0.646	0.357	0.646	0.415	0.973	0.354	0.474

The results with maple differ in several respects from those with birch; the two are not, however, strictly comparable, as those with maple belong to a later period of the season. The first division of the table shows that lime and phosphoric acid greatly diminish as the season advances. The second division shows that potash decreases with elevation, while lime, magnesia, and phosphoric acid somewhat increase. The relation of root sap to trunk sap, shown in the third division, is quite similar to that seen in birch.

In order to compare the ash of the sap with that of other parts of the tree, the percentage composition of the pure ash of two of the specimens of birch sap is given below; it may be compared with Schroeder's ash analyses of birch wood and bark already given (page 806). Beyer's analyses of the ash of hornbeam sap, and of the spring buds from the same tree, are also shown.

Birch Sap. April 20-21.

	K ² O	Na ² O	CaO	MgO	Fe ² O ³	Mn ² O ³	P ² O ⁵	SO ³	Cl	CO ² in crude ash
Lower sap	19.25	2.43	52.68	14.65	.28	—	6.14	5.12	1.46	32.90
Upper sap	36.95	1.94	32.96	13.31	.34	—	7.79	2.75	1.96	29.46

Hornbeam Sap.

Spring sap	18.11	—	42.85	11.74	3.52	6.97	6.34	8.40	1.98	30.41
Spring buds	23.56	—	21.42	11.19	.75	2.67	28.14	8.97	2.53	21.20

The ash of the upper sap in birch contains a larger proportion of potash than the ash of any of the solid parts of the tree, but it is relatively poor in phosphoric acid. Maple sap is even richer in potash than birch sap. The hornbeam sap contains much less potash than the sap of birch growing on the same soil, but, curiously, about eight times as much manganese. The ash analysis of the young buds shows in what proportion the various ash-constituents are removed for leaf formation, and strikingly illustrates the great demand for phosphoric acid in a growing tissue.

3. THE LEAF.

The investigations made upon the leaves of forest trees are extremely numerous. The composition of beech-leaves in various stages of growth has been investigated by Zöller (*Jahresb. Agr. Chem.* 1864, 86), and Rismüller (*ibid.* 1873-4, i. 253), and beech and Scotch pine leaves by Dulk (*ibid.* 1875-6, i. 134). Stöckhardt has made

leaves (*Ann. Chim. Phys.* [5], viii. 486). Sestini has analysed elm-leaves (*Jahresb. Agr. Chem.* 1875-6, ii. 6). Mulberry leaves have been investigated by O. Karmrodt (*ibid.* 1858, 62; 1868-9, 163), Th. Gohren (*ibid.* 1865, 199), E. Reichenbach (*ibid.* 1867, 68), Bechi (*ibid.* 1868-9, 163), Heidepriem (*ibid.* 1864), and F. Sestini (*ibid.* 1870-72, ii. 14).

The composition of a leaf undergoes so much alteration during its lifetime, that it is impossible to compare the leaves of different trees with each other, except when the analyses have all been made at the same time. Stöckhardt has analysed a great variety of leaves collected from the same forest on July 29; the percentage composition of the dry substance was as follows:

	Albuminoids	Non-nitrogenous extractive matter.	Fibre	Ash
White alder, <i>A. incana</i>	17.76	52.99	24.75	4.50
Lime, <i>T. parvifolia</i>	14.86	61.37	16.18	7.32
Maple	14.86	64.56	15.50	5.08
Hazel	14.60	65.85	14.50	5.15
Oak, <i>Q. pedunculata</i>	14.36	67.70	13.40	4.54
Willow, <i>S. Caprea</i>	12.37	62.68	18.50	6.48
Elm, <i>U. effusa</i>	11.71	61.50	19.15	7.64
Ash	11.21	65.94	13.70	9.15
Birch	10.96	67.42	18.10	3.52
Beech	10.64	61.43	23.75	4.18
Aspen	10.08	66.70	18.20	5.02
Black alder, <i>A. glutinosa</i>	9.13	73.49	13.25	4.13
Hornbeam	7.81	72.11	14.80	5.28

The feeding value of leaves is very considerable; nearly all the leaves mentioned above would be superior in this respect to meadow hay.

Before discussing in detail the composition of leaves, it will be well to show the nature of the changes which take place during life. Rissmüller's very complete investigation of beech leaves gave the following results:

1,000 fresh beech leaves contained in grams:

	May 7	June 11	July 14	Aug. 11	Sept. 11	Oct. 27	Nov. 18
Water	174.71	158.70	187.70	130.90	134.76	156.05	134.06
Dry substance	53.22	106.76	145.36	134.90	121.56	105.67	112.16
Albuminoids	15.03	20.21	28.07	24.02	17.39	12.68	8.76
Fat	1.25	2.58	2.64	2.71	5.88	5.85	6.66
Extractive matter	26.77	56.02	71.89	66.04	61.39	53.27	55.30
Fibre	7.69	22.38	31.92	29.93	26.06	22.45	28.62
Ash	2.48	5.55	10.82	12.18	10.81	11.41	12.80
Potash	0.77	1.20	1.28	1.19	1.14	0.87	0.74
Lime	0.36	1.38	3.02	3.90	3.26	3.57	4.21
Magnesia	0.19	0.63	0.99	1.02	0.88	0.79	0.91
Phosphoric acid	0.53	0.46	0.56	0.66	0.45	0.36	0.14
Silica	0.04	0.58	1.76	2.33	1.97	2.55	2.96

1,000 parts of fresh beech leaves contained:

Water	766.5	597.9	563.6	492.8	525.8	596.3	544.6
Dry substance	233.5	402.1	436.4	507.4	474.2	403.7	455.5

1,000 parts of dry substance contained:

Albuminoids	282.50	189.37	193.12	178.12	143.12	120.00	78.12
Fat	23.60	24.20	18.20	20.10	48.40	55.40	59.40
Extractive matter	502.60	524.73	494.58	489.58	505.08	504.10	493.08
Fibre	144.60	209.70	219.60	221.90	214.40	212.50	255.20
Ash	46.70	59.00	74.50	90.30	89.00	108.00	114.20
Potash	14.58	11.31	8.84	8.86	9.37	8.28	6.60
Lime	6.78	12.93	20.81	28.96	28.86	33.80	37.60
Magnesia	3.57	5.95	6.85	7.59	7.25	7.55	8.20
Phosphoric acid	9.93	4.39	3.91	4.09	3.77	3.47	1.24
Silica	0.87	5.44	12.13	17.31	16.28	21.15	26.44

100 parts of crude ash contained:

Potash	31.23	21.74	11.85	9.81	10.53	7.67	5.78
Soda	3.28	1.32	0.37	0.83	1.16	1.58	1.35
Lime	14.96	24.25	27.82	32.08	30.37	31.69	32.98
Magnesia	7.65	11.44	9.18	8.40	8.15	7.00	7.18
Ferric oxide	0.76	0.99	0.78	0.84	1.17	0.56	0.52
Phosphoric acid	21.27	8.43	5.24	4.53	4.24	3.22	1.08
Silica	1.87	10.47	16.26	19.17	18.23	22.36	23.15

Leaves contain the greatest proportion of water in their youngest stage of growth; after this is passed the percentage of water is chiefly dependent on the relations between supply and evaporation.

The first division of the table shows that the beech leaves increased rapidly in dry substance till July, and from that time began gradually to lose weight. As soon as the leaf is fully developed its function becomes exclusively to supply organic material for the plant, and it not only ceases to grow itself, but as autumn comes on a considerable part of its own substance is withdrawn into the parent stem.

Green leaves are rich in starch; starch is continually formed by them, and transferred from them to the branches and trunk, where it is converted into woody tissue, or stored up for use in the following spring. According to Fliche and Grandeau, the proportion of starch in the leaf is greatest at the commencement of autumn, but then rapidly diminishes, very little being left in the leaf when it falls from the tree. The proportion of sugar in green leaves is apparently considerable; Gohron found a large quantity in mulberry leaves.*

Cellulose, with its accompanying lignose, diminishes but little in the leaf after full growth has been attained, and consequently increases somewhat in percentage as other ingredients of the leaf diminish.

The quantity of tannin in beech leaves reaches its maximum, according to Dulk, in August, and remains constant till November; the percentage in the dry matter increases during nearly the whole life of the leaf. Handtke, on the other hand, found that the proportion of tannin in oak leaves diminished as the season advanced. The percentage of tannin in the dry substance was as follows:

	June 26	July 26	Aug. 25	Sept. 26	Oct. 26	Nov. 7
Beech leaves	1.16	1.80	2.40	2.93	2.80	3.68
	June 1	July 21	Aug. 5			
Oak leaves	12.87	9.94	7.43			

Fat, wax, and resinous matter are sometimes present in leaves to a considerable extent, but have been little investigated. Rissmüller found a yellow fat in beech leaves, which increased both in absolute and relative quantity during the whole lifetime of the leaf, forming in November nearly 6 per cent. of the dry substance. Gohron found in mulberry leaves from 18.4 to 19.8 per cent. of fat in the dry substance.

Respecting the nitrogenous constituents of leaves, we can only speak of the total amount. In the beech leaves investigated by Rissmüller the maximum quantity of nitrogen was present in July; after which time a great diminution took place, the nitrogenous matter being transferred to the growing parts of the trunk and branches. The proportion of nitrogen in the dry substance is extremely high in the youngest leaf, and steadily diminishes during the whole lifetime. Many leaves contain far more nitrogen than the beech we have taken as our illustration; in mulberry leaves 3 per cent. of nitrogen in the dry substance is apparently common, and in very young leaves 5-6 per cent. has been found. The percentage of nitrogen and ash found by Stöckhardt in dry oak and larch leaves was as follows:

	May	June	July	August	September	October
Oak leaves:						
Nitrogen	4.13	2.43	2.23	1.57	1.12	1.08
Ash	5.70	4.11	4.19	4.60	5.40	5.20
Larch leaves:						
Nitrogen	4.60	2.92	1.71	1.10	1.14	0.88
Ash	5.05	3.81	4.60	3.53	4.56	4.60

The absolute quantity of ash in beech leaves rapidly increases till July or August, in the case of Rissmüller's investigation, and then remains at near its maximum till the autumn. The percentage of ash in the dry substance increases through nearly the whole life of the leaf. This increase in the proportion of ash does not, however, take place in the case of all leaves, as is shown by the example of oak and larch just quoted; it depends a good deal on whether some one ash-constituent, generally lime or silica, is being steadily stored up. Fliche and Grandeau found the percentage of ash in dry acacia leaves increase from 6.25 to 11.74 per cent. between May and October, and the ash of birch leaves from 3.84 to 4.68 per cent., while leaves of cherry and chestnut, from the same forest, showed a slight diminution of ash during this period. The changes in the composition of the ash are very similar for all leaves, and are of great interest.

The table shows that in beech leaves the absolute quantity of phosphoric acid

* The quantity was 24.7-30.1 per cent.; but whether this is per cent. of the total dry substance, or per cent. of the non-nitrogenous extractive matter, is not made clear.

scarcely increases at all during growth, and that as soon as autumn commences a large part is withdrawn from the leaves to be stored up for use the next season. The investigation of Dulk on beech leaves shows that the proportion of sulphuric acid is affected in a similar manner. The quantity of potash in the leaf increases to a small extent during growth, but, like phosphoric acid, it diminishes again towards the end of autumn. The two most important ash-constituents thus increase but little in quantity during the life of the leaf, and are more or less withdrawn from it as winter approaches. It is quite otherwise with lime, magnesia, and silica; these very considerably increase with the age of the leaf, and are not withdrawn from it in autumn. We have thus in spring a young leaf extremely rich in nitrogen, phosphoric acid, and potash; while in autumn the old leaf is poor in these constituents, but rich in organic calcium salts, and with its tissues incrustated with silica. The proportions in which lime and silica occur in autumn leaves depend greatly on the character of the soil; the same kind of tree may yield on one soil a leaf ash rich in lime and containing little silica, and on another soil an ash abounding in silica and containing relatively little lime. According to A. Vogel, the assimilation of silica by a plant depends greatly on the amount of humus present in the soil.

To show that similar changes in the relation of the ash-constituents take place in the leaves of evergreen trees, we will quote the results obtained by Dulk with Scotch pine. He gathered boughs of this tree in July, and separated the leaves, according to their position on the branch, into leaves of one, two, three, and four years old; the latter age is about the extreme limit reached by leaves on this tree. In 1000 parts of dry substance he found:

	One year old	Two years old	Three years old	Four years old
Potash	8.04	3.92	4.00	3.74
Lime	2.88	4.09	5.89	7.61
Magnesia	0.77	0.97	1.79	—
Ferric oxide	1.04	1.97	1.57	1.69
Manganese oxide	1.34	1.71	1.47	2.66
Phosphoric acid	5.17	2.14	2.27	1.92
Sulphuric acid	1.35	0.82	0.76	—
Silica	0.19	0.34	0.53	1.11
Total pure ash	20.83	15.58	18.47	20.82

The following analyses of various leaves will serve to complete this part of the subject. The analyses of acacia, cherry, chestnut, and birch are by Fliche and Grandeau. The analyses of larch leaves are by R. Weber. The 'ash in dry' is pure ash in Weber's analyses; in the other cases the authors have omitted to state its nature.

	Ash in dry	K ² O	Na ² O	CaO	MgO	Fe ² O ³	Mn ² O ³	P ² O ⁵	SO ²	SiO ²	CO ² in crude ash
Acacia:											
May 2	6.25	30.60	6.37	20.82	9.67	0.91	trace	21.16	7.39	3.72	5.08
July 3	7.75	19.20	5.71	48.64	11.02	1.43	trace	8.69	3.63	1.67	21.62
Oct. 13	11.74	3.25	1.34	72.00	6.16	1.46	10.64	1.90	2.93	1.68	28.30
Cherry:											
April 28	7.80	32.78	1.89	30.57	7.82	0.95	4.42	15.80	4.34	1.41	17.60
July 3	7.30	17.80	6.44	38.06	18.38	1.29	5.62	8.20	2.46	1.76	20.07
Oct. 2	7.24	11.82	5.00	44.05	17.79	1.19	13.25	3.81	0.79	2.30	23.88
Chestnut:											
May 1	4.60	31.85	2.39	18.41	9.16	0.50	11.84	15.31	4.98	1.59	7.34
Oct. 12	4.55	10.52	2.59	49.50	6.90	2.17	12.52	8.35	2.75	4.67	13.22
Birch:											
April 30	3.84	25.54	0.43	28.72	4.40	0.72	15.87	17.46	5.19	1.73	7.92
Oct. 9-15	4.68	2.88	4.57	50.76	16.41	1.18	9.81	8.63	3.21	2.54	18.20
Larch:											
Oct. 15	3.57	23.55	1.73	14.65	8.50	3.06	—	23.70	3.15	21.66	0.64
Nov. 25 *	3.99	4.57	1.36	21.98	6.91	2.80	—	3.74	1.62	57.02	4.80

* The leaves collected at this date had fallen from the tree.

The leaf-stalk is remarkably rich in ash. Wolff's analyses of the leaf-stalk and leaf of horse-chestnut will be found in this Dictionary, iii. 173.

When leaves wither prematurely from excessive heat and drought in summer, their change in composition is not nearly so complete as in the gradual autumn withering. According to G. Kraus, such leaves retain the greater part of their nitrogen and phosphoric acid, but a considerable part of the potash, and the whole of the starch, is transferred to the tree. The loss of valuable constituents to the tree is thus greater in cases of premature withering.

Church has lately shown (*Chem. News*, xxxvi. 237) that a remarkable difference exists in the composition of the white and green parts of variegated leaves. He experimented on maple leaves (*A. Negundo*) collected Sept. 17; on leaves of holly collected Sept. 24; and on leaves of ivy collected Oct. 4:

100 parts of fresh leaves contained :

	Maple		Ivy		Holly	
	Green	White	Green	White	Green	White
Water	72.70	82.83	66.13	78.88	62.83	74.14
Organic matter	24.22	15.15	31.63	18.74	35.41	23.66
Ash	2.08	2.02	2.24	2.38	2.47	2.20
1000 parts of dry substance contained :						
Potash	14.22	62.97	11.85	53.19	10.68	30.03
Lime	45.04	12.80	32.11	14.54	22.45	18.29
Magnesia	5.36	4.64	0.69	1.25	1.59	2.75
Phosphoric acid	9.93	17.14	2.56	12.03	4.75	8.00
Total crude ash	112.82	117.64	66.14	112.69	65.21	85.07

The white portion of the leaf contains in every case a larger amount of water than the green portion. The dry matter of the white portion is richer in nitrogen, but poorer in fatty matter than the green. The proportion of the ash-constituents in the variously coloured tissues is very remarkable. The green portion of the leaf shows the usual autumn characteristics, containing comparatively little potash and phosphoric acid, but a high proportion of lime. The white part of the leaf is, on the other hand, extremely rich in potash; it contains a larger proportion of phosphoric acid, and but little lime. The total amount of ash-constituents is also greater in the white leaf. The circumstances which determine this striking difference in composition have yet to be sought in further investigation. For Church's later investigation, see *Transactions Chem. Soc.* 1879.

Both the size and the composition of a leaf are greatly affected by climate. As elevation increases, and the tree becomes less luxuriant, the leaf becomes smaller, and its percentage of ash less; the proportion of nitrogen and water will also probably decrease. R. Weber collected beech leaves at the beginning of August from forests of various elevation :

Height above sea, meters	Surface of 1000 leaves, square meters	Per cent. ash, in dry*
132	3.414	—
237	2.128	6.97
324	2.112	6.70
514	1.674	4.96
685	1.500	5.32
1043	1.083	2.84
1344	0.910	3.94

Weber found that the small amount of ash yielded by the leaves of elevated regions was far richer in phosphoric and sulphuric acids, and also in potash, than the ash of leaves at a lower level; the ash from the latter leaves was, on the other hand, richer in lime and silica. The small leaves of elevated regions are clearly in a less mature condition than those produced in a more genial climate, and this more backward state of development is apparently the chief cause of their difference in composition.

* Not being able to refer to the original (*Allgemeine Forst- u. Jagdzeitung*, 1876, 521), the writer is uncertain whether these ash-percentages belong to the leaves collected in August; they, however, undoubtedly refer to leaves from the same forests.

Weber also determined the ash in larch leaves from different elevations, and found the same diminution of ash with increased elevation; the ash of leaves at 1068 meters' height was about one-half that of leaves at 117 meters. The phosphoric acid and potash, however, in this case appeared to diminish with the diminishing proportion of ash.

Illustrations of the effect of soil upon the composition of leaves have been already given, see p. 810.

4. THE BLOSSOM, FRUIT, AND SEED.

The researches on this part of the subject have been very limited. Church has made a partial analysis of the female blossom of the elm, collected after it had fallen from the tree. 1000 parts of dry substance contained:

Nitrogen	Potash	Lime	Phosphoric acid	Sulphuric acid	Silica	Total ash
33.1	23.9	11.4	9.7	13.4	1.0	81.5

The proportion of nitrogen and phosphoric acid in the blossom is similar to that in young leaves; the proportion of potash and sulphuric acid is remarkably high.

E. Wolff determined the ash-constituents present in the various parts of horse-chestnut blossom with the following results. 100 parts of pure ash contained as follows:

	Pure ash in dry	K ² O	CaO	MgO	P ² O ⁵	SO ³	SiO ²	Cl	CO ² in crude ash
Blossom stalk	9.36	64.08	9.20	1.31	17.08	3.52	0.73	5.13	17.64
Calix and ovary	5.18	61.72	12.26	5.87	16.63	3.73	1.68	2.37	22.10
Corolla	4.78	61.22	13.62	3.84	16.97	—	1.44	3.76	21.64
Stamens	5.15	60.73	13.77	3.09	19.52	—	0.74	2.78	21.50

The ash of all parts of the blossom is seen to be extremely rich in potash, and to contain a considerable amount of phosphoric acid. The different portions of the flower are very similar both in the amount and character of their ash-constituents, but the stalk contains a double quantity of all the more important constituents, a fact similar to that already observed in the case of leaves.

The composition of some of the fruits of forest trees is given in the following table. As the percentage of water in the fresh fruit is not given in some analyses, and in others the fruit had obviously lost water before examination commenced, the results have all been calculated on the dry substance, and the highest percentage of water given in a side column:

	Number of analyses	Water in fresh	Albuminoids	Fat	Carbo-hydrates	Fibre	Ash
Acorn, with shell	6	42.00	5.80	4.53	75.98	11.57	2.32
" kernel	5	42.34	6.38	4.55	81.12	5.60	2.35
" shell	1	25.00	2.44	0.93	59.12	35.45	2.06
Chestnut, with shell	1	54.61	8.51	3.95	80.47	4.92	2.15
" kernel	3	48.75	14.32	2.58	76.32	3.32	3.45
Horse-chestnut		49.20	12.60	2.75	76.19	5.71	2.75
Walnut, kernel	4	44.50	22.52	56.94	16.04	1.44	3.06
Hilbert, kernel	1	48.00	16.15	54.81	21.35	4.81	2.88

The table illustrates the composition of two great classes of seed, in one of which—as in acorn and chestnut—the reserve of carbonaceous matter is in the form of starch; while in the other—as in walnut—it is in the form of fat.

The following ash-analyses of fruit and seed are taken from E. Wolff's *Aschen Analysen*, with the exception of the analysis of larch seed, which is by Anderson (*Highland Soc. Trans.* 1851, 26).

	Pure ash in dry	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Mn ₂ O ₃	P ₂ O ₅	SO ₂	SiO ₂	Cl	CO ₂ in crude ash
Acorn, whole	—	63.64	0.73	6.98	5.01	0.63	—	12.93	5.55	1.17	2.92	13.69
Chestnut, kernel	2.38	56.69	7.12	3.87	7.47	0.14	0.16	18.12	3.85	1.54	0.52	21.17
" shell	1.68	2.53	14.21	19.74	24.07	0.87	1.39	9.39	3.39	3.51	4.54	18.95
Horse-chestnut, unripe fruit	3.70	56.77	—	9.93	2.24	—	—	20.83	3.66	0.76	4.77	16.75
" ripe kernel	2.76	61.74	—	11.46	0.58	—	—	22.81	1.66	0.19	2.01	17.86
" green shell	5.50	75.91	—	8.81	1.14	—	—	5.28	1.61	0.57	9.72	24.55
Walnut, whole	—	28.46	—	22.24	7.35	0.75	—	36.68	2.34	1.16	0.38	2.93
" kernel	—	31.11	2.25	8.59	13.03	1.32	—	4.73	—	—	—	—
" shell	—	23.10	2.74	30.57	4.13	5.34	—	4.73	14.96	14.43	—	5.41
Beechnut, kernel	3.65	17.15	5.21	18.39	14.15	0.98	7.55	30.52	2.45	2.70	0.56	2.63
" shell	1.43	1.32	24.44	49.57	3.50	0.98	9.46	2.17	1.81	2.94	2.44	35.50
Black Alder, fruit	1.71	28.98	1.07	25.28	11.68	4.72	0.72	14.07	4.00	5.38	0.10	—
Scotch Pine, seed	4.15	22.38	1.26	1.86	5.09	3.01	—	45.96	—	10.44	—	16.71
Silver Fir, seed	4.47	21.75	7.06	1.54	16.77	1.31	—	39.61	—	11.71	0.35	—
Larch, seed	—	33.65	1.49	3.39	10.88	1.52	—	39.84	2.59	5.93	0.76	0.42

In the ash of the chestnut kernel Districh found 1.16 per cent. of alumina, and in the ash of the shell 6.86 per cent.

The ash of a seed is generally small in quantity, less for instance than that of leaves or bark; but it is high in quality, containing generally a larger proportion of phosphoric acid than the ash of any other part of the plant, and being also rich in potash. It is interesting to observe the wide difference between the ash of the shell and kernel. The former is very small in quantity, and contains far less phosphoric acid, and also less potash than the ash of the kernel, but is, on the other hand, rich in lime, and sometimes also in silica. The green or fleshy covering of the seed contains more ash-constituents than the hard shell, and is generally rich in potash.

5. THE FOREST LITTER.

Forest litter consists mainly of dead leaves, but will contain also the bark, branches, and seed vessels which fall from the trees. If left undisturbed it may become mixed to a more or less considerable extent with moss and lichen. Where fern, heather and other low-growing plants prevail, these also will contribute to the forest litter. The quantity of leaf litter annually produced has been carefully determined on 87 experimental sites in the Bavarian forests; the results are given in Ebermayer's *Gesammte Lehre der Waldstreu*. The average quantities found were as follows:

Description of forest	Number of annual determinations	Weight of air-dry litter in pounds per acre
Beech, 30-39 years old	74	3734
" 60-90 "	47	3655
" over 90 "	49	3611
Spruce fir, 30-60 years old	74	3539
" 60-90 "	52	3014
" over 90 "	53	2922
Scotch pine, 25-50 years old	55	3033
" 50-75 "	31	3117
" 75-100 "	27	3776

The amount of litter varied much in individual years, and was much greater in some forests than in others. It is the custom in many of the German forests to remove at least half of the litter, and to employ it on the neighbouring farms for the bedding of animals, and as manure. The following table shows the average weight of air-dry litter in pounds per acre when it is left to accumulate for various periods; the determinations were made at the Bavarian stations already referred to:

Age of litter	Beech	Spruce fir	Scotch pine
One year	3667	3158	3308
Three years "	7287	6778	8024
Six years "	7553	8384	12258
Many years	9301	12872	16321

Beech litter rapidly suffers decomposition; the six years' litter is little more than twice the weight of one year's deposit. Decomposition proceeds at a much slower rate in the case of fir or pine litter, the accumulations in pine forests thus become in time very considerable. The three years' and older litter of pine forests will, however, include a certain quantity of moss. Where the forest is not sufficiently close, but admits air and light freely to the soil, there litter will not greatly accumulate, nor is a thick layer of vegetable soil formed; oxidation under these circumstances takes place rapidly, and the valuable ingredients of the litter are speedily assimilated by the vegetation which takes possession of the soil.

Recently fallen leaves contain 30-50 per cent. of water. When completely air-dried, forest litter will contain 12-15 per cent. water.

The proportion of nitrogen in some of the component parts of forest litter has

been determined by Krutzsch (*Chem. Ackermann*, 1866, 158), and the nitrogen in moss by R. Hofmann (*Land. Vers.-Stat.* i. 269); but no complete investigation of the nitrogen in litter has been made. Krutzsch found the following percentages of nitrogen in the dry matter of fallen leaves, &c.:

Spruce fir leaves	1.35
" " twigs	0.57
" " cones	0.37
Scotch pine leaves	1.89
Larch leaves	0.88
Beech leaves	0.60-1.24
Oak leaves	1.05

Hofmann found the percentage of nitrogen in dry moss to be:

Hypnum cristanastrensis	1.74
" rusciforme	1.51
" triquetrum	1.45
" tamariscinum	1.44
" cupressiforme	1.37
" splendens	1.31
" silvestre	0.98
Climacium dendroides	1.75
Polytrichum commune	1.07

The proportion of the various ash-constituents in forest leaf litter is shown in the following table; the composition of forest humus, the final product of litter, is also given for comparison. The analyses are taken from Ebermayer's *Die gesammte Lehre der Waldstreu*, with a few additions from Dulk (*Land. Vers.-Stat.* xviii. 205).

1000 parts of dry substance contain—	Number of analyses	Pure ash	K ² O	Na ² O	CaO	MgO	Fe ² O ³	P ² O ⁵	SO ²	SiO ²
Beech leaf litter:										
Highest percentages		99.1	8.31	1.78	34.81	6.92	5.47	5.85	2.54	60.80
Lowest percentages		40.3	0.91	0.10	10.99	1.98	0.66	1.28	0.53	5.95
Mean	23	55.9	2.81	0.56	24.49	3.50	1.73	2.98	1.10	18.37
Oak leaf litter:										
Highest percentages		72.5	4.16	2.78	27.14	6.02	1.85	3.06	2.17	30.46
Lowest percentages		43.9	1.64	0.30	17.07	1.94	0.30	2.10	0.75	10.85
Mean		55.1	3.28	1.28	22.68	3.80	1.03	2.05	1.51	18.83
Spruce fir leaf litter:										
Highest percentages		101.9	2.42	1.40	38.50	4.19	1.93	3.84	1.18	57.40
Lowest percentages		31.1	0.05	0.22	5.36	0.74	0.22	1.26	0.43	3.86
Mean	18	45.3	1.61	0.56	20.27	2.32	0.93	2.14	0.70	16.54
Larch leaf litter	1	40.0	1.83	0.54	8.79	2.76	1.03	1.50	0.65	22.81
Silver fir leaf litter:										
Highest percentages		52.7	4.54	0.68	38.67	3.05	1.70	4.08	1.04	4.99
Lowest percentages		19.9	1.06	0.37	6.23	1.18	0.22	2.19	0.78	0.51
Mean		37.9	2.63	0.53	24.28	2.52	1.08	2.80	0.93	2.35
Scotch pine leaf litter:										
Highest percentages		20.9	2.44	1.03	10.31	2.53	1.10	1.54	0.99	2.73
Lowest percentages		10.7	0.95	0.19	2.67	0.73	0.13	0.60	0.42	1.39
Mean	12	14.7	1.61	0.61	5.82	1.61	0.49	1.11	0.67	2.12
Humus, beech forest	1	43.2	1.53	0.26	10.22	8.54	8.97	2.79	1.86	20.03
" fir forest	1	44.0	2.19	0.39	23.39	1.76	2.50	4.19	1.76	7.80

The percentage composition of the ash of leaf litter is shown in the next table.

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	Number of analyses	Pure ash in dry	100 parts of pure ash contain—							
			K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₂	SiO ₂
Beech leaf litter :										
Highest percentages		9.91	11.8	2.5	66.4	13.4	10.5	9.1	5.9	52.2
Lowest percentages		4.03	1.5	0.2	25.2	3.0	1.4	2.3	1.0	14.2
Mean	25	5.66	4.8	1.0	44.0	6.4	3.0	5.3	2.1	32.5
Oak leaf litter										
Highest percentages		7.25	9.2	3.8	48.6	13.7	2.6	8.1	4.4	42.0
Lowest percentages		4.39	3.4	0.6	35.4	4.0	0.6	3.8	1.7	24.7
Mean	3	5.51	6.1	2.1	41.0	7.5	1.8	5.6	2.8	32.5
Spruce fir leaf litter :										
Highest percentages		10.19	5.6	2.5	70.9	9.0	5.4	8.6	2.3	60.2
Lowest percentages		3.11	1.9	0.5	18.6	2.0	0.4	2.5	1.0	11.0
Mean	18	4.53	3.8	1.2	44.0	5.3	2.3	5.1	1.6	36.2
Larch leaf litter	1	4.00	4.6	1.4	22.0	6.9	2.6	3.7	1.6	57.0
Silver fir leaf litter :										
Highest percentages		5.27	16.3	2.3	78.9	12.7	3.5	20.5	3.9	10.5
Lowest percentages		1.99	2.2	1.0	31.3	2.4	0.8	4.5	1.8	4.1
Mean	5	3.79	8.3	1.5	59.3	7.5	2.6	8.3	2.4	7.7
Scotch pine leaf litter :										
Highest percentages		2.00	20.5	7.2	58.6	14.2	10.2	12.1	5.1	19.7
Lowest percentages		1.07	6.6	1.4	22.0	6.5	1.0	4.3	2.9	7.9
Mean	11	1.47	11.0	4.4	38.7	10.2	3.6	8.3	3.7	14.6
Humus, beech forest	1	4.32	3.5	0.6	23.7	5.9	9.7	6.5	4.3	46.4
" fir forest	1	4.40	5.0	0.9	53.2	4.1	5.7	9.5	4.0	17.7

Alumina and manganese oxide are commonly present in the leaf litter of fir and pine forests.

We have already seen (page 817) that the proportion of ash in leaves may be greatly influenced by the elevation above the sea level; the same influence affects both the proportion of total ash, and of phosphoric acid in leaf litter.

Ebermayer gives the composition of litter from several elevations; the following are examples: Beech-leaf litter from 1040 meters above the sea contained in 1000 parts of dry matter 40.3 of pure ash, and 1.77 of phosphoric acid; while from the lower level of 130 meters, the total ash amounted to 99.1, and the phosphoric acid to 5.85. Spruce fir litter showed less regular variations of the total ash than beech, but a considerable alteration in the phosphoric acid. At 935 meters spruce fir litter yielded 37.5 of pure ash, and 1.81 of phosphoric acid; while at 490 meters it contained 48.3 of ash, and 3.84 phosphoric acid. The litter from Scotch pine shows least variation in the proportion of phosphoric acid of all the litters examined.

The other influences which affect the composition of leaf litter are the character of the soil, and the age of the litter. The respective proportions of lime and silica are greatly dependent on the character of the soil; a calcareous soil will produce a leaf litter rich in lime and poor in silica, while on a siliceous soil the reverse will be the case. The very variable amounts of lime and silica in the analyses already quoted are chiefly due to this cause.

The effect of age upon the composition of forest litter has been little studied. Schroeder has shown that fresh beech-leaf litter treated with water loses 52.6 per cent. of its potash, 55.3 per cent. of its sulphuric acid, 19.7 per cent. of phosphoric acid, and 19.6 per cent. of magnesia, but only 4.5 per cent. of lime. The first effect of rain on litter is thus to remove potash, and increase the proportion of lime. The percentage of total ash in the litter may also rise, if the oxidation of the organic matter proceeds more rapidly than the solution of the ash. The following table shows analyses by Dulk of beech-leaf litter one and three years old, both from the same forest; also analyses quoted by Ebermayer of recent beech litter, and of beech humus, both from the same forest.

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1000 parts of dry substance contain—

	MgO									
Beech litter, one year	52.4	1.27	0.16	18.28	1.98	5.47	3.29	1.28	1.15	19.08
" three years	61.6	0.91	0.10	27.90	2.07	2.01		1.40	1.35	21.99
Beech litter, one year	48.3	2.62	0.81	17.00	4.60	1.73		4.23	0.84	14.97
Humus from same forest	1.63	0.26	10.22	2.54	3.97			2.79	1.86	20.03

100 parts of the ash contain :

Beech litter, one year old	2.44	0.32	35.12	3.81	10.51	6.32	2.46	2.22	36.67
" three years old	1.48	0.16	45.30	3.36	3.26	5.84	2.28	2.19	35.71
Beech litter, one year old	5.64	0.68	36.71	0.94	3.73		9.14	1.82	32.34
Humus from same forest.	3.52	0.59	23.67	5.88	9.20		6.47	4.30	46.37

In the Bavarian forests it is reckoned that 3-8 years are necessary for the formation of humus from the leaf litter of coniferous trees, and 2-5 years in the case of litter from deciduous trees. The presence of tannin or resinous matter retards decomposition, while lime or alkalis assist it. The decay of forest litter is to a great extent brought about by the agency of fungi.

We have already stated that moss, lichen, fern, &c., frequently contribute to forest litter. Moss is chiefly abundant in pine forests which are of sufficient age to admit light freely to the soil; it flourishes most in moist elevated situations. The growth of lichen in abundance indicates great poverty of the soil. Fern, on the other hand, is extremely rich in the more valuable ash-constituents. The following ash-analyses will serve to illustrate this part of the subject. The three analyses of *Hypnum* are from the Bavarian experiments quoted by Ebermayer, the remainder are quoted from Wolff. The two analyses of *N. Filix mas.* do not, unfortunately, refer to plants growing on the same soil.

1000 parts of dry substance contain :	Number of analyses	K ² O	Na ² O	CaO	MgO	Fe ² O ³	P ² O ⁵	K ² O	SiO ²
Moss:									
<i>Hypnum</i> , various species	21.0	7.61	1.42	5.47	2.51	1.82	4.78	1.65	4.88
<i>Sphagnum</i>	25.6	3.46	2.15		1.61	3.03	1.16	1.29	7.37
Fern:									
<i>N. Filix mas.</i> (June)	79.4	38.40	1.60	7.00	5.90	0.80	12.40	3.20	4.80
" (October)	75.6	30.09	4.01	14.17	6.26	0.73	1.94	4.08	3.31
Lichen:									
<i>C. rangiferina</i>	11.4	1.08	0.09	1.25	0.19		0.32	0.17	8.02

100 parts of the pure ash contain :

	Number of	CaO	MgO	Fe ² O ³	P ² O ⁵	SiO ²
<i>Hypnum</i> , various species	23.0	4.5	8.1	5.3	14.5	17.2
<i>Sphagnum</i>	13.6	11.8	5.9	11.8	4.5	28.8
<i>N. Filix mas.</i> (June)	48.3	8.8	7.4	1.0	15.6	6.0
" (October)	30.8	18.7	8.3	1.0	2.6	4.4
<i>Pteris aquilina</i>	19.4	12.6	2.3	3.9	5.2	48.7
<i>C. rangiferina</i>	9.5	17.0	1.0	0.2	2.8	70.8

For ash-analyses of a variety of other forest plants we must refer to Wolff's *Ashen Analyses*.

The importance of forest litter in promoting a vigorous growth of timber can hardly be overrated, the removal of litter from the forest is consequently in most cases very undesirable. Where the litter remains undisturbed it gradually forms a forest soil rich in humus. Such a soil has a great power of retaining water, in this respect all descriptions of arable soil. Where this humus soil is trees may be successfully cultivated on steep hill sides, and in stony regions,

would else suffer greatly both from drought and the effects of floods. Humus also assists greatly in the disintegration of a rocky soil, and in the solution of the mineral plant food which it contains. The decay of forest litter will also enrich the atmosphere of the forest with carbonic acid, and thus promote a vigorous vegetation. The physical properties of forest litter and of humus, hardly fall within the scope of the present article; they are fully treated in Ebermayer's excellent work already referred to.

6. THE ANNUAL REQUIREMENTS OF A FOREST.

The careful determinations made in Germany of the average produce of forests, both in wood and leaf, coupled with the analyses made of these products, enable us to calculate with more or less precision the quantity of matter annually removed by an acre of forest from the soil and atmosphere. The two following tables are quoted from Ebermayer. The first table gives the annual growth of wood, and the annual production of leaf litter, as determined at the Bavarian experimental stations; the wood is inclusive of roots.

Description of forest	Number of experimental stations	Dry matter in lbs. per acre			Leaf litter to 100 wood
		Total wood	Leaf litter	Total produce	
Beech, 30-60 years old	11	2930	3002	5932	102
" 60-90 "	7	2436	3005	5441	123
" 90-120 "	7	3099	2917	6016	94
Mean	25	2822	2975	5796	105
Spruce fir, 30-60 years old . .	12	2744	3008	5750	110
" 60-90 "	9	3345	2560	5905	77
" 90-120 "	10	3105	2483	5588	80
Mean	31	3064	2683	5748	88
Scotch pine, 25-50 years old .	10	2156	2614	4770	121
" 50-75 "	6	3535	2678	6213	76
" 75-100 "	5	2962	3244	6206	110
Mean	21	2884	2845	5730	99

The mean annual production of dry matter by the three descriptions of forest is seen to be wonderfully accordant, it averages 5755 lbs. per acre. This quantity of dry matter is considerably in excess of that yielded by average farm crops, which, except in the case of turnips, mangels, and other root crops, seldom exceeds 4000 lbs. per acre. In a forest there is an enormous development both of foliage and root, and in consequence great scope for assimilation. About one-half of the dry matter produced is in the form of leaf, which is finally returned to the soil as forest litter.

The amount of carbon in the annual produce is given by Ebermayer as follows; the figures are translated into lbs. per acre:

	Beech	Spruce fir	Scotch pine
Carbon in wood	1397	1577	1484
Carbon in leaf litter	1263	1153	1258
Total carbon	2660	2730	2742

The mean amount of carbon assimilated by an acre of forest is thus 2711 lbs. per annum; such an amount of carbon would be contained in the volume of air lying upon an acre, if the stratum of air is reckoned as 10 meters in height, and renewed fourteen times during the period of vegetation. If we assume that an adult man exhales daily 800 grams of carbonic acid, then an acre of forest will consume in a year the products of

respiration of 15.4 men. A considerable part of the carbon required by a forest will, however, be supplied by the gradual decay of the fallen leaves. The atmosphere of a forest receives from this source a special supply of carbonic acid.

The quantity of nitrogen annually demanded by an acre of forest cannot be stated with any exactness, as very few determinations of nitrogen have been made either in wood or leaf litter. Taking Schroeder's determinations of nitrogen in beech wood (p. 803), and Krutzsch's analysis of beech-leaf litter, there would be required for the annual growth of the wood 7-8 lbs. of nitrogen, and for the leaf about 30 lbs. As the nitrogen of the leaf is all returned to the soil, the requirement of a forest in nitrogen becomes extremely small, far smaller than that of ordinary farm crops; if, however, the litter is removed from the ground, the quantity of nitrogen required will be much increased.

The next table shows the quantity of the various ash-constituents required for the annual growth of an acre of forest. The ash-analyses employed for calculating the composition of beech and Scotch pine wood are by Vonhausen and Heyer; those used in the case of spruce fir are by Schroeder. The analyses of leaf litter employed are the mean results already given (see p. 821). The figures are lbs. per acre.

	Dry matter	Pure ash	K ² O	CaO	MgO	P ² O ⁵	SO ²	SiO ²
Beech, wood	2822	26.4	4.15	12.86	3.44	2.56	0.20	2.15
„ leaf	2975	16.75	8.81	73.08	10.90	9.32	3.23	53.85
Total	5797	191.9	12.96	85.94	14.34	11.88	3.43	56.00
Spruce fir, wood	3064	20.1	3.62	8.16	1.81	1.29	0.64	2.88
„ leaf	2683	121.3	4.30	54.37	6.20	5.72	1.87	44.25
Total	5747	141.4	7.92	62.53	8.01	7.01	2.51	47.13
Scotch pine, wood	2884	14.8	2.32	8.96	1.52	0.95	0.23	0.49
„ leaf	2845	41.5	4.32	16.84	4.28	3.28	1.51	5.83
Total	5729	56.3	6.64	25.80	5.80	4.23	1.74	6.32

The quantity of ash-constituents required by the three kinds of forest is seen to be very different. With beech, the total amount of ash is very similar to that contained by an average crop of wheat or oats; with spruce fir the quantity of ash is much smaller; with Scotch pine the demand for cinereal food is still less, not amounting to one-third of that required by beech. The preponderating constituents of all these ashes are lime and silica. When we look at the more important ash-constituents, potash and phosphoric acid, the economy of forest growth becomes still more apparent. A beech forest requires annually only half as much phosphoric acid as a wheat crop, and less than half as much potash, while the demands of the fir and pine forests are much below that of beech. The table further shows that by far the greater part of the ash is contained in the leaf-litter; if this is not removed from the forest, and the timber is felled only when full grown, the quantity of ash-constituents removed from the soil becomes infinitesimal. The growth of beech timber is seen to demand but 4.1 lbs. of potash and 2.5 lbs. of phosphoric acid; while Scotch pine requires only 2.3 lbs. of potash and about 1.0 lb. of phosphoric acid. With these very small supplies of cinereal food, the forest will produce 3000 lbs. of dry matter in the form of timber. The forest is thus unequalled for the production of large growths with small supplies both of ash and nitrogen; this economy is speedily marked in the case of Scotch pine, which is excellently suited for cultivation on poor siliceous soils. The economy of the forest is greatly promoted when the leaf litter is left undisturbed.

The statements just made refer to forests grown for timber, and felled after many years' growth; the annual requirements of seedling trees, thickly planted in a nursery, are far more considerable. Dulk (*Landw. Versuchs.-Stat.* xvii. 175) has determined the composition of various seedling trees growing on the same soil. The following table shows the quantity of ash-constituents contained in an acre of seedlings. The seedling beech and Scotch pine were one year old; the seedling spruce fir examined were one, two, and four years old. As the one year spruce was unusually feeble, the figures given below are in this case the half of those belonging to the two years old plant. The Scotch pine and spruce fir were planted at the rate of about 10,000,000

per acre, the beech at the rate of 2,000,000. The following figures are pounds per acre:

	Dry matter	Pure ash	K ² O	CaO	P ² O ⁵	SiO ²
Beech seedlings	5152	135	27.2	46.5	16.7	10.9
Spruce fir seedlings	5254	133	29.2	38.4	20.6	15.5
Scotch pine seedlings	3934	96	25.2	17.6	18.7	11.8

The consumption of potash and phosphoric acid is thus greater in the young plant than in the mature tree, but the demand for lime and silica is less.

Further information on some of the subjects connected with trees will be found in articles *BEECH*, *BIRCH*, *CHESTNUT*, and *HORSE-CHESTNUT*, in this Dictionary.

R. W.

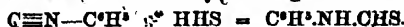
FORMALDEHYDE, CH₂O. This compound is formed by the action of the silent electric discharge on a mixture of hydrogen and carbon dioxide: CO₂ + 2H₂ = CH₂O + H₂O (Brodie, *Proc. Roy. Soc.* xxii. 171).

For the preparation of formaldehyde, J. Volhard (*Liebig's Annalen*, clxxvi. 128) recommends—instead of Hofmann's apparatus (1st *Suppl.* 622), in which explosions often take place,—a Davy's glow-lamp (i. 74, 1093) fed with wood-spirit. Over the lamp is placed a glass tube, which fits loosely to the neck, and is connected by its upper end with a condenser, a receiver, several wash-bottles containing water or ammonia, and finally with an aspirator. The stream of air should be so regulated that the platinum spiral surrounding the wick shall not exhibit a glow perceptible by daylight. With this apparatus, about 90 to 100 grams of liquid can be collected in twenty-four hours. The liquid thus produced gives a bright speculum with ammoniacal silver nitrate, even at the heat of the hand. When evaporated with ammonia it leaves a residue of hexamethylenamine. On saturating it with hydrogen sulphide, leaving it for some days, and repeating the treatment, it is converted into a thick white pulp, from which thioformaldehyde, C²H²S², can easily be obtained (1st *Suppl.* 622; 2nd *Suppl.* 1156).

Hofmann finds that the quantity of formaldehyde in the liquid obtained by the use either of this or his own original apparatus never exceeds 1 per cent., but that a much stronger solution may be obtained by passing a mixture of methyl alcohol and air through a rather narrow platinum tube containing a bundle of thin platinum wires, and applying a gentle heat. Streams of formaldehyde vapour then escape from the tube, and yield, when condensed, a liquid containing 5 per cent. of formaldehyde. The apparatus, when properly fitted up and supplied with the mixture of air and methyl alcohol, may be kept in a state of glow for several months. Moreover, by distilling off the methyl alcohol which condenses at the same time—which may be done without much loss of formaldehyde—freezing the liquid several times, and then removing the ice, a solution is obtained in which the proportion of formaldehyde amounts to 10 per cent. (*Deut. Chem. Ges. Ber.* xi. 1685, Sept. 1878).

On the Compounds of Formaldehyde with Aromatic Hydrocarbons, see 2nd *Suppl.* 583.

FORMANILIDE (THIO-), C⁶H⁵N²S = C⁶H⁵.NH.(CHS). *Phenyl-thioformamide* (A. W. Hofmann, *Deut. Chem. Ges. Ber.* x. 1095).—Phenyl isocyanide, placed in a large vessel filled with hydrogen sulphide, is transformed in the course of a few days into a crystalline mass of *thioformanilide*, which may at once be obtained in the pure state by dissolving it out with ether and crystallising it from boiling water:



As, however, the preparation of pure phenyl isocyanide is rather troublesome, it is better to prepare the thioformanilide from the crude product of the action of chloroform on aniline in presence of an alcoholic solution of potash. On mixing this product with a saturated alcoholic solution of potassium sulphide, and leaving it for some hours, a considerable quantity of the thioanilide is formed, together with other substances; and on pouring the alcoholic solution into water, an oil is deposited, containing—besides the thioformanilide—phenyl isocyanide, methenyldiphenyldiamine, and unaltered aniline and chloroform. This liquid is treated with hydrochloric acid to remove aniline, and the residue after exposure to the air to allow the chloroform to evaporate, is dissolved in boiling water, and filtered. On cooling the thioformanilide crystallises out, whilst the methenyldiphenyldiamine remains in solution as hydrochloride.

Pure thioformanilide crystallises in long, colourless needles which melt at 137.5° with partial decomposition, splitting up into phenyl isocyanide and hydrogen sulphide.

Its aqueous solution is intensely and persistently bitter. It dissolves readily in cold dilute alkaline solutions, and is precipitated unchanged on the addition of an acid; but on heating the alkaline solution, the thio-compound is decomposed, with formation of an alkaline sulphide and formate, and liberation of aniline.

Thioformanilide, $C^6H^5.NH(CSH)$, bears the same relation to the isomeric compound, thiobenzamide, $C^6H^5.CS.NH^2$, that the isonitril, $C^6H^5-N\equiv C$, bears to the nitril, $C^6H^5-C\equiv N$.

FORMIC ACID, $H.CO.OH$. *Formation.*— α . By passing a mixture of marsh-gas and air over a platinum spiral ignited by the voltaic current. No formaldehyde is produced at the same time (Coquillon, *Compt. rend.* lxxvii. 444). β . By the action of the silent electric discharge on a mixture of hydrogen and carbon dioxide, $CO^2 + H^2 = CH^2O^2$ (Brodie, *Proc. Roy. Soc.* xxi. 245). γ . By oxidation of trimethylamine with permanganate (Wallach & Clauser, *Deut. Chem. Ges. Ber.* viii. 1237). δ . By the action of ammonia on glyoxal (Lubavin, *ibid.* 768).

On the preparation of Formic acid by distilling Oxalic acid with Glycerin and other Polyatomic Alcohols, see Lorin (2nd Suppl. 620; further *Ann. Chim. Phys.* [4], xxix. 367; *Bull. Soc. Chim.* [3], xx. 241; xxiv. 436; xxv. 217, 519; *Jahresb. f. Chem.* 1873, 526; 1875, 504; 1876, 515; *Chem. Soc. Jour.* 1873, 1219; 1874, 140; 1875, 1250; 1876, i. 560; ii. 59).

Estimation.—According to Portes & Ruyssen (*Compt. rend.* lxxxii. 1504), formic acid may be estimated volumetrically by mixing 5 grams of sodium acetate and 9 grams of mercuric chloride, with 2.5 grams of the mixture under examination, and 200 c.c. of water; heating the liquid on the water-bath; diluting it to 500 c.c.; filtering; and titrating the undecomposed mercuric chloride with solution of potassium iodide.

Electrolysis.—According to N. Bunge (*Deut. Chem. Ges. Ber.* ix. 1598), formic acid, when electrolysed, yields hydrogen at the negative pole, and carbon dioxide, with or without oxygen, at the positive pole. The volumes of the three gases are as 2 : 2 : 1. Bunge supposes that the group CHO^2 , set free in the first instance at the positive pole, reacts with H^2O so as to form CH^2O^2 and free oxygen, which then oxidises the formic acid to CO^2 and H^2O ; and he considers that this view is supported by the fact that the amount of CO^2 produced is greater as the conditions of the experiment are more favourable to oxidation (diminished strength of current, increased surface of electrodes, varying density of the electrolyte).

Reaction with Polyatomic Alcohols.—From experiments on the action of formic acid on erythrite and glycol, Henninger concludes that the reduction of a polyatomic alcohol by formic acid is preceded by the formation of its formate, if the latter cannot take place, then also there is no reduction. In every case of reduction, a polyatomic alcohol loses two hydroxyl-groups; thus, glycol yields ethylene; glycerin yields allyl alcohol; erythrite yields, first an unsaturated glycol, $C^6H^5(OH)$, then a hydrocarbon, C^6H^6 (Henninger, *Bull. Soc. Chim.* [2], xxi. 242).

Reaction with Oxalic acid.—Concentrated formic acid, heated to 195° with dehydrated oxalic acid, gives off CO^2 and CO in the proportion of 1 : $1.2-3$; and since oxalic acid, when heated alone, gives off equal volumes of the two gases, it follows that the excess of carbon monoxide must arise from the decomposition of the formic acid. The same resolution into carbon monoxide and water takes place when formic acid is heated with 1 mol. anhydrous potassium or sodium formate, beginning at 120° , and going on regularly between 150° and 155° , carbon monoxide being given off and dilute formic acid distilling over. At the end of the distillation, the residual formate has the same weight as at the commencement of the experiment, and may be used for the decomposition of a fresh quantity. Formate of barium and the other formates do not exhibit this property. Formic acid reacts in exactly the same way with dry acetate of potassium or sodium, the acid which distils over then containing acetic as well as formic acid (Lorin, *Bull. Soc. Chim.* [2], xxv. 217).

Metallic Formates. *Potassium formate*, in aqueous solution is decomposed by a current of an indifferent gas, e.g. carbon dioxide, air or hydrogen, at $80^\circ-90^\circ$, with evolution of formic acid (Naudin & Montholon, *Compt. rend.* lxxxiii. 345).

Calcium Formate.—According to Lieben & Liebermann & von Zetta (2nd Suppl. 583), this salt subjected to dry distillation yields formaldehyde, which, when treated with sodium-amalgam, yields a small quantity of methyl alcohol. It appears, however, from later experiments by Lieben & Paternò (*Gazz. chim. Ital.* iii. 290), and by Friedel & Silva (*Compt. rend.* lxxvii. 1546) that methyl alcohol is a direct product of the dry distillation of calcium-formate. Among the products there also occurred an oil insoluble in water, which, after purification by repeated distillation, gave by analysis numbers agreeing approximately with either of the formulae $C^6H^{10}O$, or $C^6H^{12}O$, and having, at all events, a high molecular weight.

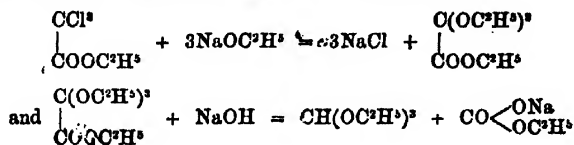
Formic Ethers. *Methyl Formate*, $\text{H.CO}^2\text{OH}^1$.—The following is an advantageous method of preparing this ether. A saturated solution of hydrogen chloride in wood-spirit,—which should be freshly prepared, as it decomposes after a while with formation of methyl chloride—is distilled with a metallic formate, preferably the calcium salt, in the proportion of 100 parts of the salt to 130 parts of the saturated alcohol. The alcoholic solution is allowed to drop into a flask containing the formate, and connected with a condenser, as the reaction is violent; the flask should be well shaken after each addition of alcohol. The distillate is neutralised, and dried by calcium chloride. The mass thus obtained, which consists of a crystalline compound of the ether with the chloride, is then heated on a water-bath; the parts first distilling are rejected as containing chlorine, whereas the later portions of the distillate are very nearly free from chlorine. The ether obtained has a sp. gr. of 0.9928 at 0° , and a boiling point of 30.4° at 712 mm.

Methyl formate has also been obtained by the action of alcoholic hydrogen chloride on hydrogen cyanide, but this reaction is very violent and not well adapted for the preparation of the ether.

When the vapour of methyl formate is passed through a red-hot tube, it is for the most part resolved into carbon monoxide and methyl alcohol: $\text{CH}(\text{CH}^3)\text{O}^2 = \text{CO} + \text{CH}^3\text{O}$, a smaller portion yielding carbon dioxide and probably methane (J. Volhard, *Liebig's Annalen*, cxxxvi. 128).

Ethyl Formate, $\text{CH}(\text{C}^2\text{H}^5)\text{O}^2$.—A mixture of this ether with ethyl iodide treated with zinc yields diallyl-carbinol, $(\text{C}^2\text{H}^5)^2\text{CHOH}$, together with diallyl (p. 632). Diallyl carbinol is also formed when ethyl formate is treated with a mixture of ethyl and allyl iodides in presence of zinc (Kafonnikoff, *Liebig's Annalen*, cxxxv. 148).

Triethyl Formate, or *Ethyl Orthoformate*, $\text{CH}(\text{OC}^2\text{H}^5)^3$, is produced, together with sodium carbonate and ethyl carbonate, by heating ethyl trichloracetate with sodium ethylate, a reaction which doubtless requires the presence of water (sodium hydroxide), and may be represented by the equation



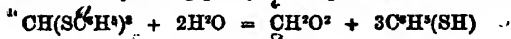
(H. Klien, *Jenaische Zeitschrift*, [2], iii. 2 *Supplementheft*, 63).

Orthothioformic Ethers are produced by heating the aqueous solutions of the sodium-derivatives of the corresponding mercaptans with chloroform, e.g.



Ethyl Orthothioformate is a mobile, pale yellow liquid, having a repulsive and persistent alliaceous odour. It is partially decomposed by distillation. Fuming hydrochloric acid resolves it into ethyl-mercaptan and formic acid.

Phenyl Orthothioformate, $\text{CH}(\text{SC}^6\text{H}^5)^3$, prepared in like manner, crystallises in short white prisms, which melt at 39.5° , and dissolve in ether, benzene, nitrobenzene, glacial acetic acid, and carbon sulphide. It is decomposed by fuming hydrochloric acid at 100° in sealed tubes, yielding phenyl-mercaptan and formic acid:



(Gabriel, *Deut. Chem. Ges. Ber.* x. 190).

The *formic ethers of polyatomic alcohols* (formina) are obtained by heating these alcohols (glycerin, erythrine, &c.) with oxalic acid. When heated to about 136° , they are easily decomposed, with evolution of carbon monoxide, which may thus be readily obtained in the pure state (Lorin, *Compt. rend.* lxxiii. 629; *Bull. Soc. Chim.* [2], xiv. 389; *Chem. Soc. J.* 1876, ii. 58).

FORMORTHOLOLUMINE. See TOLUIDINES.

FOX-GLOVE. See DIGITALIS (p. 647).

ACID, $\text{C}^1\text{H}^1\text{O}^1$. See 2nd Suppl. 554.

FRANKLINITE. G. H. Seyms (*Sill. Am. J.* [3], xii. 210) has analysed several specimens of this mineral, with the view of determining whether the variation in the amount of iron which occurs in it affects the ratio of monoxides to sesquioxides,

and consequently its relation to the spinel group. The first experiments were made on perfectly formed crystals from Mine Hill, the mean of the analyses giving:

SiO ²	FeO ²	Mn ² O ³	MnO	ZnO
0.17	63.40	4.44	10.46	23.11 = 101.58.

The relation of the metals to the oxygen calculated from this analysis would be—

	Metals	Oxygen
Fe ²	44.38	19.02
Mn ²	3.09	1.35
Mn	8.10	2.36
Zn	18.55	4.56
		20.37
		6.92

Dividing by the atomic weights, the ratio of metals to oxygen would be R : O :: 3 : 3.999, nearly equal to R²O³, or an oxygen-ratio of the monoxides to sesquioxides of 1 : 0.981, or nearly 1 : 1, corresponding with the formula of the spinel group, (R²O³ + RO = R²O³). The state of the oxidation of the manganese was determined by dissolving the mineral in hydrochloric acid, and estimating the liberated chlorine by Bunsen's iodine method, the mean of these results being 0.46, which requires the presence of 4.44 per cent. of Mn²O³.

A second sample gave, as a mean of four analyses—

SiO ²	Al ² O ³	FeO ²	FeO	ZnO	MnO
0.08	0.65	67.42	15.65	6.78	9.53 = 100.11

giving as the relation between the metals and the oxygen:

	Metals	Oxygen
Al ²	0.35	0.30
Fe ²	47.19	20.23
Fe	12.17	3.48
Zn	5.44	1.34
Mn	7.38	2.15
		20.53
		6.07

These numbers lead to the atomic ratio R : O :: 1 : 1.331, or 3 : 3.994 = R²O³, and show the oxygen-ratio of monoxides to sesquioxides to be 1 : 0.981, or nearly 1 : 1.

The results of the analyses give in both cases a ratio very nearly corresponding with that of spinel, notwithstanding the great differences in the relative amounts of iron, zinc, and manganese.

Pseudomorphs after calcspar, consisting of a mixture of franklinite with manganic hydroxide, have been analysed by H. B. Cornwall (*American Chemist*, 1873, iv. 127), with the following result:

Fe ² O ³	Mn ² O ³	ZnO	CaO	MgO	K ² O, Na ² O	H ² O	CO ₂	SiO ²
14.627	58.387	5.285	4.739	1.253	traces	11.293	3.488	0.170 = 99.242.

* Other determinations gave 12.777 and 16.129 per cent.

See SELENIUM-DISMUTH-GLANCE.

A hydrated manganous silicate from the manganese mine of Adervielle in the Louron valley, Hautes-Pyrénées. It occurs, sometimes in sugar-like groups of small hexagonal plates, with distinct cleavage parallel to the face OR, sometimes massive. Sp. gr. = 4.07. Hardness = 4.5 to 5. Colour, red. Transparent to translucent. Analysis gave

SiO ²	MnO†	MgO CaO	H ² O
36.12	53.05	2.96	6.87 = 100

† With small quantity of iron.

leading to the formula 4MnO.3SiO₂.2H²O (E. Bertrand, *Compt. rend.* lxxxiii. 229).

FRUIT. On the Estimation of Citric and Tartaric Acids in Fruit-juices, see page 508.

On the Detection of Fuchsin or Rosaniline therein. See ROSANILINE.

On the Fermentation of Fruits. See FERMENTATION (p. 778).

See SUGAR.

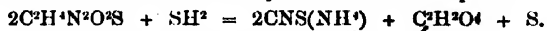
FUCHSINE. See ROSANILINE.

FULMIGUANURATES. See the next article.

FATES, C²N²M²O³, and FULMINATES, C²N²M²O³ (A. Steiner, *Dent. Chem. Ges. Ber.* vii. 1244; viii. 618; ix. 779). 1. Action of Hydrogen Sulphide on Mercuric Fulminate.—When dry hydrogen sulphide is passed into anhydrous

ether in which mercuric fulminate is suspended, there is formed, together with ammonium thiocyanate, a white substance having the composition $C^2H^4N^2O^2S$; it contains the elements of 1 mol. fulminic acid, or nitro-cyanomethane, $CH^2(NO^2)CN$, and 1 mol. SH^2 , and may be regarded as nitro-acethiamide, $CH^2(NO^2)-CS(NH^2)$. The ethereal liquid filtered from mercuric sulphide contains a portion of the nitro-acethiamide in solution, and on spontaneous evaporation leaves that substance, together with an aqueous solution of ammonium thiocyanate and oxalic acid, which contains free sulphur in suspension, and after a while deposits long crystals of oxalic acid. To obtain the nitro-acethiamide free from sulphur, it is rinsed several times with water, till the water, which is at first milky from suspended sulphur, runs away quite clear, and the nitro-acethiamide is washed with water on a filter till the wash-water no longer exhibits the thiocyanate reaction. This first portion of the compound, obtained from the ethereal solution under which the fulminate has been decomposed, is, however, less pure than the latter portions, which are extracted from the mercuric sulphide by the use of fresh ether.

Nitroacethiamide crystallises in microscopic prisms insoluble in water, moderately soluble in alcohol and ether, from which however it can be obtained only by spontaneous evaporation, as it decomposes, with separation of sulphur, at temperatures below the boiling point of ether. It is quickly decomposed when gently heated with water, and still more quickly by aqueous ammonia, into carbon dioxide, ammonium thiocyanate, and free sulphur. Treated in ethereal solution with *hydrogen sulphide*, it is resolved into oxalic acid, ammonium thiocyanate, and free sulphur:



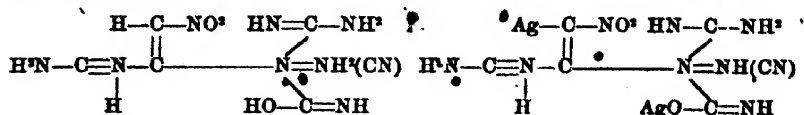
Heated with *chloride of lime*, it yields *chloropicrin*.

Action of Ammonia on Mercuric Fulminate.—This salt, treated with aqueous ammonia, yields urea, guanidine, and two nitro-compounds of high molecular weight, represented empirically by the formula $C^2H^{12}N^{10}O^2$. One of them, which is amorphous, is obtained, in the form of a mercury-compound; the other is obtained in the free state, and forms small needles. When the action takes place at 70° under pressure, a third nitro-compound, $C^2H^{11}N^9O^2$, crystallising in needles, is produced. This last body dissolves easily in warm, sparingly in cold water, is insoluble in alcohol, and forms well-crystallised salts. Heated to 150° with water or dilute hydrochloric acid, it is completely resolved into carbon dioxide and ammonia, [$? and free hydrogen: C^2H^{11}N^9O^2 + 9H^2O = 6CO^2 + 9NH^3 + H^2$]; fuming hydrochloric acid does not appear to act upon it.

Mercuric fulminate, heated to 80° in a closed vessel with *alcoholic ammonia*, yields ammonium carbonate, traces of a nitro-compound soluble in alcohol, a body containing cyanogen and ammonia, and finally basic mercuric fulminurate. A double compound of the last two substances may be extracted from the mercury precipitate by hot water. The resulting solution leaves, on evaporation, a crystalline body of curdy aspect, which, after repeated solution and evaporation, leaves the sparingly soluble basic fulminurate of mercury. This curdy substance, when treated with acids, gives off hydrogen cyanide; when decomposed by hydrogen sulphide, it yields mercuric sulphide, ammonium fulminurate, and hydrocyanic acid; and when boiled with sal-ammoniac, it yields mercuric chloride and ammonium fulminurate.

It appears then that when mercuric fulminate is heated with *alcoholic ammonia*, it yields nothing but fulminuric acid, whereas, when heated with *aqueous ammonia*, it yields urea, guanidine, and the complex substances above mentioned. Hence it appears probable that fulminuric acid is likewise formed in this latter reaction, but that, instead of appearing in the free state or in the form of ammonium salt, it enters into combination with the guanidine present, or with guanidine-residues, giving rise to these complex bodies, which, according to this view, should be derivatives of fulminuric acid, $C^2H^{12}N^{10}O^2$. And, in fact, when the body $C^2H^{12}N^{10}O^2$ is dissolved in alcoholic ammonia in a sealed tube to about 120° , till it was completely dissolved, it yielded, together with CO^2 and NH^3 , a brown flocculent body, which is likewise obtained under similar circumstances from fulminuric acid. Moreover, the alcoholic solution contained a large quantity of guanidine. The same result was obtained with the modification of the body $C^2H^{11}N^9O^2$ which crystallises in needles. A further proof that these bodies are derivatives of fulminuric acid is afforded by the fact that when treated with strong sulphuric acid, they yield products identical with those which are obtained by the action of sulphuric acid on ammonium fulminurate, viz. carbon dioxide and oily nitracetonitril. If the reaction be continued till the evolution of carbon dioxide ceases, and the clear yellowish solution be diluted with water, crystalline nitracetonitril is immediately precipitated, identical with that which is obtained in like manner from ammonium fulminurate (see NITRO-ACETONITRILS). The sulphuric acid solution also contains a large quantity of a

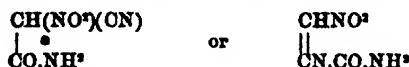
These bodies may therefore be very probably regarded as fulminurates containing guanidine residues united by the nitrogen of the cyanogen, which has become quinivalent. The body, $C^8H^{11}N^3O^3$, and its silver salt, may perhaps be represented by the following formulae:



The bodies $C^8H^{11}N^3O^3$ contain an additional group CNNH^2 .

These compounds may be called fulmiganurates, $C^8H^{11}N^3O^3$, which contains three guanidine-residues, being distinguished as *fulmitriguanurate*, and $C^8H^{11}N^3O^3$, which contains four such residues, as *fulmitetraguanurate*.

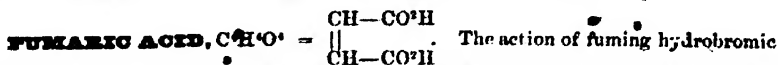
Steiner suggests for fulminuric acid the constitutional formula



Double Salts of Mercuric Fulminate.—A compound of this salt with potassium cyanide, $C^8N^3O^2\text{Hg.ONK}$, is obtained in needle-shaped crystals by adding the fulminate to a warm concentrated solution of potassium cyanide, filtering the greenish-yellow solution, and leaving it to cool. It dissolves easily in cold water and in alcohol. The aqueous solution decomposes at a certain degree of concentration, with a decrepitating noise and deposition of a hard green substance. The solution mixed with a dilute acid in sufficient quantity to decompose the potassium cyanide deposits pure mercuric fulminate.

A similar compound with potassium thiocyanate, $C^8N^3O^2\text{Hg.CNSK}$, crystallises in laminae, slightly soluble in cold water, decomposed by hot water. The corresponding ammonium salt, $C^8N^3O^2\text{Hg.CNS}(\text{NH}^2)$, also crystallises in laminae (Steiner).

Iron Fulminurate?—A salt thus designated is produced, according to E. W. Davy (*Chem. News*, xxxiii. 47), by the action of metallic iron on mercuric fulminurate suspended in water, mercury being then precipitated and a purple salt remaining in solution. If the iron be partly precipitated from this solution by an acid, there remains a liquid which, on addition of dilute acids, assumes a splendid red colour. The same coloration is produced when a solution of potassium ferrocyanide is added to water in which mercuric fulminurate is suspended, and the resulting liquid is heated or mixed with a dilute acid. Hence Davy concludes that in both cases a salt is formed having the composition of ferroso-potassic fulminate, $\text{FeK}(\text{C}^8\text{N}^3\text{O}^2)^2$, and that this salt is converted by acids into an acid iron salt, $\text{FeH}(\text{C}^8\text{N}^3\text{O}^2)^2$ [ferrosohydric fulminate]. Neither of these salts is stable in the dry state.

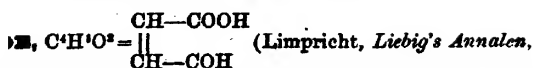


acid on this acid and on maleic acid has been examined by Fittig and Dorn (*Deut. Chem. Ges. Ber.* ix. 192, 1191; *Liebigs Annalen*, clxxxvii. 42). Fumaric acid, heated with concentrated hydrobromic acid in sealed tubes at 100° , is converted into monobromosuccinic acid, apparently identical with that formed by the action of bromine on succinic acid. When boiled with water the brominated acid is almost entirely re-converted into fumaric acid. Maleic acid or anhydride, in fine powder, dissolves quickly in cold fuming hydrobromic acid, and is almost immediately converted into fumaric and monobromosuccinic acids in equal numbers of molecules.

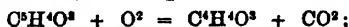
The bromosuccinic acids formed in this manner from fumaric and maleic acids are identical. The two acids, when treated with sodium-amalgam, likewise yield the same product, viz. ordinary succinic acid, $\text{CO}^2\text{H}-\text{CH}^2-\text{CH}^2-\text{CO}^2\text{H}$, but with bromine they yield different products. These facts are not consistent with the supposition that maleic acid is a saturated compound represented by the formula $\text{CH}^2=\text{C}(\text{COOH})^2$, but they are completely accounted for if maleic acid be regarded as an unsaturated compound containing two free combining units, and represented by

the formula $\begin{array}{c} \text{CH}^2-\text{CO}-\text{OH} \\ || \\ \text{C}-\text{CO}-\text{OH} \end{array}$. This view likewise accounts for the fact that maleic acid takes up hydrobromic or hydrochloric acid much more readily than fumaric acid.

FUMARIC ALDEHYDE—FURFURAL.



clxv. 253), is formed, with evolution of carbon dioxide, by the action of chromic acid mixture on pyromucic acid :



also by the action of bromine (2 mols.) and water on pyromucic acid (1 mol.):



The bromine in the proportion just mentioned is taken up and decolorised, even at ordinary temperatures; and if the solution, either directly or after removal of the hydrobromic acid by silver oxide, be agitated with ether, and the ether then left to evaporate, there remains a syrup from which the compound $\text{C}^4\text{H}^4\text{O}^2$ sometimes crystallises out over sulphuric acid after a week or a fortnight, sometimes not at all; on the other hand, the brominated liquid, if heated on the water-bath, yields fumaric acid. The indistinctly crystalline compound $\text{C}^4\text{H}^4\text{O}^2$ may be regarded as fumaric aldehyde, since it appears to yield fumaric acid when treated with silver oxide, and precipitates metallic silver when heated with silver solution and ammonia. Its aqueous solution gives with neutral lead acetate a white precipitate, which dissolves when heated. When neutralised with baryta-water it remains colourless, but is coloured yellow by an additional drop; and on further addition of baryta-water, and boiling, it yields a yellow precipitate, which, like that precipitated by alcohol from the nearly neutral solution, has the composition $(\text{C}^4\text{H}^3\text{O}^2)^2\text{Ba}$. The original compound $\text{C}^4\text{H}^4\text{O}^2$ may be separated from it. With *sodium-amalgam* the compound $\text{C}^4\text{H}^4\text{O}^2$ gave in one experiment $\text{C}^4\text{H}^4\text{O}^2$, in another $\text{C}^4\text{H}^4\text{O}^2$. It does not unite with alkaline bisulphites, but forms a brown resin with ammonia in ethereal solution (see further p. 836).

FUNGI. The presence of oxalic acid, which, in the form of hydropotassic oxalate or of calcium oxalate, has been regarded by some chemists as a common constituent of fungi—has been demonstrated in about 30 species by the experiments of Hamlet a. Plowright (*Chem. News*, xxvi. 93; *Chem. Soc. J.* 1877. ii. 796). One of the most remarkable examples of strong acidity in a fungus was afforded by *Fistulina hepatica*, which was found to contain 0.083 per cent. of free oxalic acid. The constitution of this plant was found to be as follows:

	Water	86.120
Volatile constituents	Oxalic acid	0.08
	Fat	0.15
	Woody fibre (cellulose)	2.03
	Mycose	12.984
	Extractive matter	
Mineral constituents (ash)	Resin	0.896
	Silica	
	Ferric oxide	
	Lime	
	Magnesia	
	Potash	
	Phosphoric acid	
	Sulphuric acid	100.000
	Chlorine	

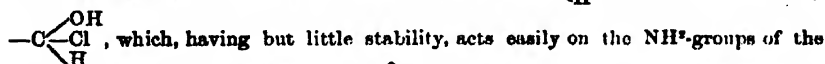
WITWATE, or *Metacellulose*. See PLANT-TISSUE.

FURFURAL or **FURFUROL**, $(\text{C}^4\text{H}^4\text{O}^2)$. *Pyromucic Aldehyde*.—This compound may be obtained from wood by heating with water under pressure. When wood in small chips or shavings is heated for four hours with water to about 198° , an acid liquid is obtained, yielding, by distillation, methyl alcohol and an oil which boils between 186° and 216° , and may be separated by cooling with a freezing mixture into two layers, the upper of which appears, from its odour and composition, to be a mixture of turpentine-oil and cymene, while the lower, when subjected to fractional distillation, yields furfural boiling at 163° – 171° . The crude oil, of which 10 ounces were obtained from 100 pounds of wood, contains about 42 per cent. of furfural. Wood boiled with water under ordinary pressure does not yield furfural (C. Greville Williams, *Chem. News*, xxvi. 231, 293). H. Müller (*ibid.* 247) likewise observed the formation of furfural by strongly heating wood with water.

According to Gudkow (*Zeitschr. f. Chem.* 1870, 360) bran, digested with dilute sulphuric acid, is completely exhausted of the constituents which yield furfural, and

after digestion with caustic potash, yields but little of that compound. Cellulose, gum-arabic, and wheat-starch do not yield furfural. When pigs are fed with bran, the furfural-yielding substance passes into the dung, and appears not to be digested.

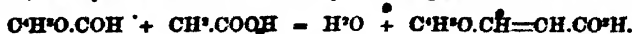
Reaction of Urea with Furfural (Hugo Schiff, *Deut. Chem. Ges. Ber.* x. 773-776). Most aldehydes act easily on aqueous or alcoholic solutions of urea, forming condensed ureas, but furfural appears to have no action upon such solutions. It acts, however, in a peculiar manner on solutions of urea nitrate, a violet colour being produced, which gradually disappears, with deposition of a black substance. The colour is not occasioned by the nitric acid. Aqueous solutions of furfural are not coloured by dilute mineral acids, except after the furfural has begun to decompose, when they certainly have this effect. Now although neither acid nor urea alone colours pure furfural, a very characteristic change occurs when the two substances react together. If a solution of urea in about 3 parts of concentrated furfural-solution be treated with a few drops of concentrated hydrochloric acid, the liquid becomes warm and then gradually of a splendid purple-violet colour, and finally solidifies to a brownish-black mass. This effect is produced in alcoholic solutions. Aqueous furfural solutions after some days, even if kept in the dark, acquire the property of becoming coloured by mineral acids. If hydrochloric acid of sp. gr. 1.1 be employed, a pale-red colour appears in about ten minutes, but if a small crystal of urea be dissolved in this solution, a deep violet colour is formed in a few minutes, slowly changing to brown and depositing a black substance. The reaction, which is very delicate, has also been obtained with the slightly soluble polyureides of the aldehydes, and with urine. With many amides, as acetamide, benzamide, oxamide, thiocarbamide, mono- and diphenylthiocarbamide, taurine, glycocine, creatine, cyanuric acid, uric acid, alloxan, oxaluric acid, parabanic acid, the reaction is not produced; but it takes place with allantoin, though perhaps somewhat more tardily and less intensely than with urea. The hydrochloric acid acts in such a manner that the aldehyde group $-\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{H} \end{smallmatrix}$ changes into the group



urea, with formation of water, and reproduction of hydrochloric acid, just as in the case of aldehyde-condensations effected by small quantities of hydrochloric acid. A result indicating the occurrence of such a reaction is observed when rather more hydrochloric acid is used, and the experiment is conducted as follows: A very small crystal of urea in a small dish is covered with a drop of highly concentrated aqueous furfural solution, and a drop of hydrochloric acid of sp. gr. 1.10 is at once added. A change of colour occurs very rapidly, passing through yellow, green, and blue into violet, the latter in a few minutes changing to a splendid purple-violet. This change of colour is quite different from that which altered furfural-water would undergo without the addition of urea. The reaction is extremely delicate, the tint becoming so intense that in ten minutes the solution may be diluted with 50 to 80 times its bulk of water, and yet retain its colour most definitely. The black substance separating in this latter case is amorphous, like carbon, and insoluble in ordinary solvents. After washing with water and drying at 110° it contains hydrogen and nitrogen. It is supposed to be a humus-like body, which has carried down some urea with it, to which it obstinately adheres.

The difference between the behaviour of furfural and that of other aldehydes to urea and other amides, is observable also in the reaction of furfural with basic amines. Most aldehydes react with aniline and toluidine in such a manner that water separates, and the diatomic aldehyde-residue takes the place of the hydrogen of the NH_2 -group: $\text{C}^6\text{H}_5\text{NH}_2 + \text{C}^6\text{H}_5\text{O} = \text{H}_2\text{O} + \text{C}^6\text{H}_5\text{N}=\text{C}^6\text{H}_5$ (1st *Suppl.* 79), whereas, according to Stenhouse, 2 mols. of aniline or toluidine unite directly and without separation of water, with 1 mol. of furfural, to form basic bodies (2nd *Suppl.* 1178).

Furfuracrylic Acid, $\text{C}^6\text{H}_5\text{O}^2 = \text{C}^6\text{H}_5\text{O}-\text{CH}=\text{CH}-\text{COOH}$, the group $\text{C}^6\text{H}_5\text{O}$ being called 'Furfury' (Baeyer, *Deut. Chem. Ges. Ber.* x. 355). This acid, metameric with salicylic acid, and analogous in constitution to the homologues of cinnamic acid discovered by Perkin (p. 500), is produced by a process similar to that which gives rise to the latter, viz. by the action of acetic anhydride and sodium acetate on furfural:



When 1 pt. furfural is heated to boiling with 2 pts. sodium acetate and 4 pts. acetic anhydride for eight hours, the solution on cooling solidifies to a crystalline mass, which dissolves almost completely in warm aqueous sodium carbonate, the solution yielding with acids a precipitate of furfuracrylic acid in the form of large yellow

3rd *Sup.*

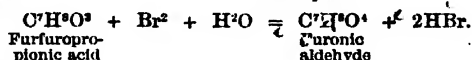
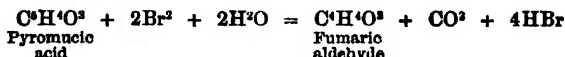
2 H

needles, in quantity nearly equal to the furfural employed. After purification with animal charcoal and recrystallisation, the acid is obtained in long colourless needles.

Furfuracrylic acid smells like cinnamon, melts at 125°, and volatilises undecomposed with vapour of water. It dissolves sparingly in cold water (about 500 parts), more freely in hot water, and crystallises immediately on cooling. Strong hydrochloric acid dissolves it with a green coloration, which is tolerably stable. Strong sulphuric acid acts in a similar manner.

Furfuropropionic Acid, $C^4H^4O^3 = C^4H^4O.CH^2.CH^2.CO^2H$, formed by the action of nascent hydrogen (sodium-amalgam and water) on furfuracrylic acid, is much more soluble in water than the latter. When extracted by ether from its aqueous solution, it remains on evaporation as a colourless crystalline mass, melting at 50°–51°, and possessing in a higher degree the peculiar odour of furfuracrylic acid. It is coloured yellow by hydrochloric acid, and, when warmed with that acid, forms a reddish-yellow solution containing a non-volatile acid, the composition of which has not yet been determined.

Furonic Acid, $C^4H^4O^3 = C^6H^4.CH=CH.CO.CH^2.CH^2.CO^2H$. The aldehyde of this acid, $C^4H^4O^3$, appears to be formed by the action of bromine on furfuropropionic acid, nearly in the same manner as fumaric aldehyde is formed from pyromucic acid (p. 832).



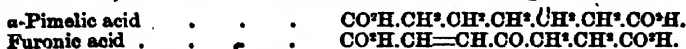
The aldehyde is, however, very unstable and not easily separated; but if the bromine mixture be at once heated with silver oxide (3 mols.), the silver salt of furonic acid is produced, according to the equation:



1.4 gram of furfuropropionic acid is dissolved, with aid of heat, in 100 grams of water, and the cooled liquid, filtered, if necessary, is mixed with an exactly weighed quantity of 1.6 gram of bromine = 1 mol.; the slightly yellow liquid, after being completely decolorised with sulphurous acid, is immediately poured into a flask containing a quantity of recently precipitated and well-washed silver oxide (= 6 mols. prepared from 11 grams of silver nitrate); the mass is digested for 2½ hours at 65°–70°; and the temperature is then raised above 70°, whereupon decomposition takes place. The progress of the oxidation may be traced by mixing a small portion of the liquid with hydrochloric acid, exhausting with ether, and heating the crystalline mass which remains after the evaporation of the ether, with strong hydrochloric acid. The first samples thus treated exhibit a red-violet coloration, but towards the end of the process this coloration is no longer produced. At the end of the reaction, the mass is mixed with hydrochloric acid and exhausted with ether till that liquid no longer acquires a yellow colour. After evaporation of the ether, the furonic acid (1 gram) remains in yellowish crystals, which may be purified by treating the hot aqueous solution with animal charcoal.

Furonic acid separates from the hot solution on cooling, in slender colourless needles, melting at 180°. It dissolves sparingly in cold water and in ether, without colour in strong hydrochloric acid, even when heated. Strong sulphuric acid dissolves it with reddish-yellow colour, changing to brown on heating. The aqueous solution, neutralised with ammonia, yields with silver nitrate a white precipitate of the salt $C^4H^4Ag^2O^3$, which is but slightly altered by boiling with water.

Furonic acid, heated to 200°–205° with hydriodic acid and red phosphorus, yields—in addition, to an oily body having the odour of the fatty acids, and probably consisting of caproic acid—crystals of a bibasic acid $C^4H^4O^3$, agreeing in all its properties with the normal or α -pimelic acid which Dale & Schorlemmer obtained from subarone (see PIMELIC ACID). Hence it follows that furonic acid belongs to the normal series:



Furonic acid, heated to boiling with baryta-water, is decomposed in the same manner as pyromucic acid, a yellow precipitate being formed, consisting of the barium compound of fumaric aldehyde (p. 832), while a volatile fatty acid, smelling like acetic or propionic acid, remains in the mother-liquor.

Hydrofuronic Acid, $C^4H^4O^3$, is formed from furonic acid by the action of water and sodium-amalgam at ordinary temperatures, or of hydriodic acid and red phos-

phorus at 160°. It is very soluble in water, and crystallises in needles melting at 112°. Its silver salt is a white precipitate moderately soluble in hot water, and turning grey on exposure to light.

By the further action of sodium-amalgam, hydrofurfuronic acid is reduced to pimelic acid, together with intermediate products.

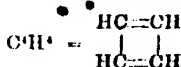
Furfurangelic Acid, $C^4H^4O^3 = C^4H^4O.CH=CH.CH^2.CH^2.CO^2H$ (Baeyer, *Deut. Chem. Ges. Ber.* x. 1364). This acid is formed by gradually heating furfural with normal butyric anhydride and sodium butyrate in an open vessel to 100°–180° for twelve hours. The resulting mass dissolves easily in hot aqueous sodium carbonate, and the solution mixed with sulphuric acid, yields furfurangelic acid as a brown mass, which may be decolorised by animal charcoal. The acid crystallises from hot water in colourless silky needles, melting at 87°–88°.

By sodium-amalgam, furfurangelic acid is easily reduced to normal furfurovaleric acid, $C^4H^4O^3 = C^4H^4O.CH^2.CH^2.CH^2.CO^2H$, a colourless oil, convertible into a crystallised acid by treatment with silver oxide.

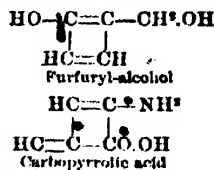
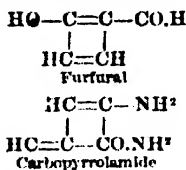
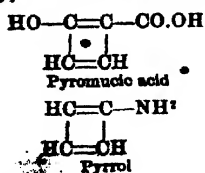
Furfurobutylene, $C^4H^4O = C^4H^4O.CH=CH.CH^2.CH^2$. The action of isobutyric anhydride and potassium isobutyrate on furfural is quite different from that of the normal anhydride; it begins at 70° with evolution of carbon dioxide, becomes more energetic as the temperature rises, and is nearly completed in four hours at 160°. The resulting brown mass contains only a small quantity of a crystallisable acid; but, on the other hand, a considerable quantity of furfurobutylene, in the form of a colourless oil which boils at 153°, and has a peculiar odour resembling that of *Carobus nycophanta*.

Furfurobutylene is the second known hydrocarbon-derivative of furfuran, C^4H^4O (*infra*), the first being the compound which Cahours obtained by the action of heat on thiofurfural (ii. 753). Cahours assigned to this body the formula $C^4H^4O^2$; but Schwanert has shown (*Liebigs Annalen*, cxxiv. 61) that it differs from thiofurfural, C^4H^4OS , only by the absence of sulphur, and has the composition C^4H^4O . It may be regarded as the stilbene of furfuran, $C^4H^4O^2 = C^4H^4O.CH=CH.C^4H^4O$.

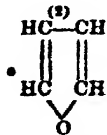
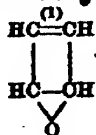
Constitution of Furfural and its Derivatives.—Limpricht (*Deut. Chem. Ges. Ber.* 1869, 211) regards these bodies as derivatives of a hydrocarbon, called tetrene,



composed of 2 mols. of acetylene, and intermediate between acetylene and benzene; thus:

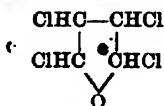


Baeyer (*Deut. Chem. Ges. Ber.* x. 1369) and R. Schiff (*ibid.* 1192; further *Ger. chim. ital.* 1878, 77) take a somewhat different view of the constitution of these bodies, regarding them as derivatives of the compound C^4H^4O (Limpricht's tetraphenol, Baeyer's furfuran), which Limpricht obtained by distilling the barium salt of pyromucic acid with soda-lime (2nd Suppl. 1032). With regard to its constitution, Limpricht has shown that it is not attacked by sodium or reduced by sodium-amalgam, and that it does not combine with alkaline bisulphites; hence it cannot be an aldehyde, ketone, or alcohol-group, or an ordinary ether-group, so that there remains for it, amongst known forms, only the type of ethylene oxide, $O \begin{smallmatrix} \diagup CH^2 \\ \diagdown CH^2 \end{smallmatrix}$ or perhaps that of vinyl oxide, $H^2C=CH-OCH=CH^2$, the first leading to formula (1), the second to (2) or (3):

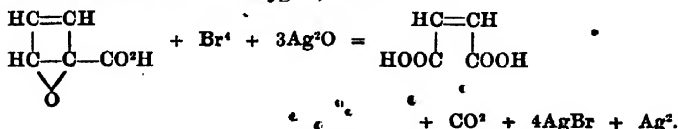


All three of these formulae are in accordance with the observation of Malaguti (iv. 765)

that ethylic pyromucate can take up 4 atoms of chlorine, forming the compound $C^2H^2Cl^4(C^2H^2O^2)$, and all three lead to the same chlorine-compound,

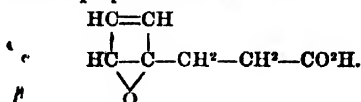


A criterion between the three formulae may be found in the fact, discovered by Limpricht, of the formation of fumaric acid by the oxidation of pyromucic acid (p. 832). When pyromucic acid is treated with bromine and water, carbon dioxide is evolved, and a body having the composition $C^4H^2O^2$ is formed, most probably consisting of fumaric aldehyde, as it reduces silver salts and appears to yield fumaric acid by oxidation. Baeyer also has obtained fumaric acid by heating a dilute solution of pyromucic acid with bromine and silver oxide. This result is easily explained if pyromucic acid be represented by a formula derived from the first of those above given for furfuran, and the separation of CO^2 be supposed to occur at the place of one of the carbon-atoms attached to the oxygen; thus:



If, on the other hand, pyromucic acid were represented by a formula derived from the second or third formula of furfuran, its conversion into fumaric acid could not take place without transposition of atoms within the molecule.

Formula (1) for furfuran is further confirmed by the mode of conversion of furfuropropionic into furonic acid (p. 834). Furfuropropionic acid requires 2 atoms of bromine to convert it into an aldehyde-compound, which may then be transformed into an acid by the action of silver oxide. Supposing now that the lateral chain is attached to a carbon-atom of furfuran which is directly connected with the oxygen-atom, the formula of furfuropropionic acid will be:

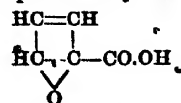


The formation of the aldehyde requires the addition of an atom of oxygen; the oxygen-atom already present remains attached to a CH-group, forming the aldehyde-group COH ; and the additional oxygen-atom attaches itself to the carbon-atom which was linked to this CH-group, forming a ketonic group CO , and at the same time the linking of the two carbon-atoms is severed. The resulting compound, furonic aldehyde, has therefore the constitution represented by the formula

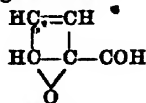


and the aldehyde, by taking up 1 at. oxygen, is converted into furonic acid, $C^4H^4O^3$.

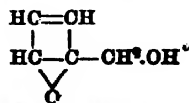
Adopting then the formula (1) for furfuran, the principal compounds of the group will be represented by the following formulae:



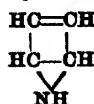
Pyromucic acid



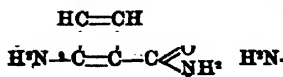
Furfural



Furfuryl alcohol



Pyrrol



Carbopyrrolamide



Carbopyrrolic acid

FURFURAMIDE, $C^4H^4N^1O^2$ (R. Schiff, *Deut. Chem. Ges. Ber.* x. 1186). This compound, prepared by the action of ammonia on aqueous furfural (ii. 746), melts

at 117° . When treated with *nitrous acid* it is at first resolved into furfural and an ammonium salt, but the reaction does not stop at that point. The ethereal solution of furfural saturated with $\text{N}^{\circ}\text{O}^2$ deposits nothing on standing, but if the ether is allowed to evaporate spontaneously, a violent reaction begins when it has nearly disappeared. The red syrupy residue grows warm, streams of nitric oxide escape, and a red oil is left, which finally solidifies, yielding a body with strongly acid properties. This phenomenon occurs only when small quantities of furfural (3 to 4 grams) are operated upon. If a larger quantity (e.g. 10 grams) is used, as soon as the ether has evaporated, a flash is suddenly observed, about 3 feet high, accompanied by steam or smoke, and a porous mass of carbon is left behind.

Action of Thiocarbimides on Furfuramide.—(1.) With allyl-thiocarbimide. The compound, $\text{C}^{14}\text{H}^{12}\text{N}^{\circ}\text{O}^2.\text{CSNC}^{\circ}\text{H}^3$, is obtained in fine silky-white needles, insoluble in water, but soluble in alcohol, partly soluble in ether, melting at 118° , and decomposing at 135° . (2.) With phenyl-thiocarbimide a well-crystallised snow-white compound is formed, consisting of $\text{C}^{14}\text{H}^{12}\text{N}^{\circ}\text{O}^2.\text{CSNC}^{\circ}\text{H}^3 + \text{H}^2\text{O}$, insoluble in water. It may be heated to 100° without loss of weight.

Aldehydes do not seem to form any compounds with furfuramide or furfurine.

FURFURINE, $\text{C}^{14}\text{H}^{12}\text{N}^{\circ}\text{O}^2$. This base, isomeric with furfuramide, is obtained by bringing the latter in contact with boiling aqueous potash (ii. 747). It melts at 116° .

Furfurine is not acted upon by nascent hydrogen (from iron filings and acetic acid), and does not unite with thiocarbimides. The experiment was tried with mustard-oil and with phenyl-thiocarbimide; but in both cases the furfurine separated out unaltered. In contact with carbon disulphide it turns red, but does not undergo any further alteration. With chloroform and alcoholic potash, it does not form any compound analogous to the isocyanides.

Acetyl-furfurine, $\text{C}^{14}\text{H}^{11}(\text{C}^2\text{H}^3\text{O})\text{N}^{\circ}\text{O}^2$, is prepared by dissolving furfurine in acetic anhydride at a gentle heat, treating the crystalline pulp which separates on cooling, with hot water, to decompose the excess of acetic anhydride, and crystallising the product from boiling alcohol. It is thus obtained as a white flocculent micro-crystalline mass, insoluble in water, and only moderately soluble in alcohol and ether. It is an extremely stable compound, not being decomposed by potash except at the melting heat. When heated alone, it turns brown at 240° , and decomposes completely with fusion, at about 260° . It has entirely lost the basic properties of furfurine, and is not dissolved by dilute acids. Strong nitric acid decomposes it, but it is not attacked by nitrous acid; neither is it acted upon by iodide of ethyl or methyl, or by sodium and boiling xylene.

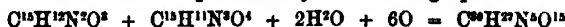
Acetyl-furfurine Hexbromide, $\text{C}^{14}\text{H}^{11}(\text{C}^2\text{H}^3\text{O})\text{N}^{\circ}\text{O}^2.\text{Br}^6$, is formed on adding 6 at. bromine to a cold solution of 1 mol. acetyl-furfurine in glacial acetic acid. The combination takes place with considerable rise of temperature, but without evolution of hydrobromic acid. It is, therefore, entirely an additive compound, and in its formation each of the three furfur-groups $\text{C}^2\text{H}^3\text{O}$ in the furfurine molecule takes up 2 atoms of bromine. On pouring the product into water, the hexbromide separates as a yellowish white substance becoming pulverulent when dried. It is soluble in glacial acetic acid, and is precipitated therefrom by water, with a somewhat deeper yellow colour. It dissolves easily in alcohol, but is partly decomposed at the same time, the alcohol acquiring a deep brown colour and taking up hydrobromic acid.

Action of Nitrous Acid on Furfurine. Nitrosfurfurine.—When potassium nitrite is added to a solution of furfurine in dilute sulphuric acid, no gas is evolved at first, but after some time, a yellowish crystalline body separates, which is insoluble in water, and in ether, but readily dissolved by alcohol, and may be purified by solution in alcohol and precipitation with ether. The body thus obtained has the composition $\text{C}^{14}\text{H}^{11}\text{N}^{\circ}\text{O}^3$. It is likewise produced by saturating an alcoholic solution of furfurine sulphate with gaseous nitrogen trioxide. If, on the other hand, a solution of furfurine in absolute ether be saturated with $\text{N}^{\circ}\text{O}^2$, and every trace of moisture excluded, a small quantity of an easily decomposable body is obtained, which becomes dark-coloured at 82° , and then slowly carbonises.

The compound $\text{C}^{14}\text{H}^{11}\text{N}^{\circ}\text{O}^{14}$ melts at 94° – 95° to a red liquid; forms a *platinochloride*, which crystallises in broad needles, moderately soluble in water, less soluble in alcohol and ether. With ammoniacal *silver nitrate*, the compound $\text{C}^{14}\text{H}^{11}\text{N}^{\circ}\text{O}^{14}$ forms a granular silver double salt, which is not in the least altered by light.

Nitrosfurfurine, $\text{C}^{14}\text{H}^{11}(\text{NO})\text{N}^{\circ}\text{O}^2$, is formed on mixing very dilute solutions of potassium nitrite and furfurine sulphate, and separates as a yellow precipitate, which, after purification by crystallisation from ether, melts at 112° . It is insoluble in water, moderately soluble in alcohol and in ether, from which it separates in large golden-yellow triclinic crystals.

The compound $C^*H^*N^*O^{13}$ appears to be formed from 1 mol. furfurine and 1 mol. nitrososulfurine in the manner represented by the following equation:



(R. Schiff, *Gazz. chim. ital.* viii. 76).

Furfurine itself is an imidogen-base, $NH(C^{13}H^{11}NO^*)$, as appears from the following considerations:

1. Only one of its hydrogen-atoms can be replaced by an alcohol-radicle, e.g. methyl, ethyl, amyl (ii. 750).
2. Its acetyl-derivative offers great resistance to the action of alkalis.
3. Nitrous acid converts it into a nitroso-derivative.
4. It does not unite with aldehydes or thiocarbimides.

On *Furfuraniline* and *Furfurotoluidine*, see 2nd Suppl. 1078.

FUSEL-OIL. For the detection of fusel-oil in ethyl alcohol, Bouvier (*Zeitsch. anal. Chem.* 1872, 343) agitates the liquid with a few small lumps of *potassium iodide*, whereupon, if fusel-oil is present to the amount of $\frac{1}{2}$ or 1 per cent., a distinct light-yellow colour is produced, arising from the decomposition of the potassium iodide. According to Böttger, on the other hand (*Dingl. pol. J.* cccvii. 516), pure amyl alcohol does not decompose potassium iodide, but this salt may be decomposed by the acids contained in spirit of inferior quality. A trustworthy method of detecting amyl alcohol in spirit of wine is to mix the liquid with a dilute solution of *potassium permanganate*, which is decolorised by amyl alcohol much more quickly than by ethyl alcohol. A. Dupré effects the oxidation with *chromic acid mixture*, and after removing the excess of chromic acid, distils off the acids produced by the oxidation. The aqueous solution of these acids is repeatedly distilled to remove as much as possible of the acetic acid, and the remaining acid is converted into barium salt. The difference between the amount of barium in the salt thus obtained and that of barium acetate, affords evidence of the presence of fusel-oil in the alcohol, and may also give an approximate estimate of its quantity (*Pharm. J. Trans.* [3], vii. 867).

On the use of *Chloroform* for the detection of fusel-oil in spirit, see page 77.

FUSTIC. On adding potassium nitrite to a very dilute decoction of fustic mixed with nitrate of toluidine (or aniline), the clear liquid becomes turbid and brownish-yellow, then orange-red, and finally deposits a vermilion-coloured precipitate. A similar reaction is exhibited by phloroglucin, maclurin, catechin, and extract of hops (Weselsky, *Deut. Chem. Ges. Ber.* ix. 216).

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